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FINAL REPORT

ON

STUDY OF COATINGS FOR IMPROVED FIRE AND DECAY RESISTANCE OF MINE TIMBERS

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FOREWORD

This report summarizes the results of a "Study of Coatings for Improved Fire and Decay Resistance of Mine Timbers", work sponsored by NASA under Contract NAS 2-9077. The program was conducted between December 1975 and May 1977.

Mr. Paul M. Sawko was the NASA Technical Monitor. The Principal Investigator for Springborn Laboratories, Inc., was Dr. Bernard Baum. Roy A. White was Project Leader, and Paul Willis was Chemist. Dr. Myer Ezrin was the supervisor of Polymer Characterization; Arthur Karszes was the supervisor of Physical Testing. Cost calculations were carried out by Mr. Tibor Gabris.

SUMMARY

The purpose of this program was to find a fire- and rot-retardant polymer/fungicide reaction product for coating mine timbers.

Fire-retardant polymers were screened as films and coatings on fir wood. Curable polyimide appeared to be flame retardant and evolved a minimum of fumes when exposed to a flame. Several organic and metal, low-toxicity, fungicides were reacted with the polyimide in-situ on the wood. These coated samples were screened for fungus resistance. All formulations rated well - even the polyimide film without additives was fungicidal. The fir wood control itself resisted internal damage during the ten weeks of fungus exposure. A more severe test for fungus resistance will be required.

Wood panels coated with polyimide containing propyl-p-hydroxy benzoate fungicide were subjected to flame tunnel testing and to the NBS smoke test. The coating definitely cut down the smoke generation but burned through readily in the flame tunnel test. However, oxygen index values of the wood were increased by 50 percent using the polyimide/propyl-p-hydroxy benzoate coating. This indicates that the polyimide-coated timbers are more difficult to ignite versus uncoated wood.

Roy A. White

Bernard Baum

INTRODUCTION

Wood timber has been used to prevent wall and ceiling collapse in mines for thousands of years. Relatively little has been done to fireproof and decay- or rot-retard the timbering in order to prevent accidents or disasters, however.

Some timber used in mines is rot- or fire-retarded. Usually the treatments utilize water-soluble ingredients, however, and the dripping water condition in most mines tends to wash out most of the active ingredients after a few years or less.

The purpose of this effort is to develop a combination flame-retardant coating with leach-resistant fungicide to be used as a coating and/or impregnant for the mine timber. The technique initially employed consisted of preparing an adduct from a suitable reactive fungicide with an agent such as formaldehyde and then reacting this intermediate subsequently with a flame-retardant polymer having appropriate reactive sites.

The initial screening indicated that Monsanto's "Skybond" polyimide was sufficiently flame retardant and relatively fume free in a torch flame.

Polyimide prepolymers with their available acid and amine sites apparently also react with many fungicides directly at the high (200^{o}C) cure temperatures. No intermediate was required to render a low rate of soxhlet-water leaching.

LITERATURE SEARCH

GENERAL

Mine timbers may be and frequently are any type of timber at hand. Douglas Fir is the most common type of timber material, however. Most timbers, especially large timber cross sections, are wedged into place. Smaller timbers may be secured to rock by means of bolts ("headers"). Life expectancy of timbers may range from 18 months for temporary support structures to 5-10 years for the thicker, permanent timbering.

FUNGUS/ROT PROTECTION

Mine conditions - 15-32°C and usually 100 percent RH - are very favorable to fungus growth. Federal regulations and MESA (Mine Enforcement Safety Association) require preservative on all timbers that are to be used for 3 years or more. It is believed, however, that many timbers in place are not so treated. Over the years, the following materials have been found useful as fungicides:

- Metals (Organic or Inorganic Salts or Complexes)

Arsenic	Copper
Tin	Mercury
Zinc (slight effect)	Antimony

- Inorganic Anions

Borate	Fluoride
Chromate	Iodine
Arsenate	

- Organic

Phenols - e.g., chlorophenols, o-phenylphenol

Quaternaries

Certain pyridine derivatives - e.g., 2,-3,-5,-6-tetrachloro-4-(methyl sulfonyl) pyridine

Salicylic acid esters - e.g., propyl hydroxy benzoate

Brominated salicylanilides

Sulfurs - e.g., N-(trichloromethyl thio) phthalimide; tetramethyl thiuram disulfide; 2-(4-thiazolyl) benzimidazole

Thiocyanate - e.g., methylene bisthiocyanate

Koppers Osmose K-33 (thought to be chromated copper arsenate) is widely used for fungus protection in the United States. Koppers can impregnate the Osmose salts (in water solution) by tapping into older, somewhat rotten wood with a pressure hose and pressuring in solution at cf 50 psi. Vacuum/pressure impregnation tanks can be used on virgin timber.

Mine timbers can be infused to some extent with fungicides on site in the mine. One method utilizes a sodium fluoride paste smeared on the timber and covered over with a type of bandage for some time while the fluoride diffuses into the wood.

Vaporizable materials such as Vapam, methyl bromide, chloropicrin, and trichloroethylene can be infused into somewhat rotted timber by injecting the chemicals at intervals into holes bored in the timber. This treatment can kill fungi in the interior of the timber but cannot be considered a permanent treatment.

Creosote is widely used in telephone pole and railroad tie impregnation but is not used in mines because of its extremely high smoke density and acrid odor in the event of fire.

The terms impregnate and infuse as used herewith are relative terms. The "impregnation" of these chemicals is generally not as deep as one might suppose. Hard woods, especially, have a low porosity and many impregnations are only superficial - e.g., 0.6 mm deep - although much deeper penetration is effected at the cut ends. The heart wood at the center of the tree is particularly low in porosity. Pine woods on the other hand are much more porous than hard wood. Excessively dry wood has been found to be difficult to penetrate with water solutions. Wet wood is much easier to penetrate. Solvent penetration is frequently feasible with drier woods.

The problem of leachability of the water-soluble fungicides has received attention. On one hand, the fungicide should be somewhat water soluble to (1) enable penetration into the wood pores as a water solution, and (2) further diffuse within the wood structure to poison the fungi wherever located. On the other hand, excessive water solubility enables removal from the wood by leaching in a dripping wet environment.

Copper borate can be dissolved with zirconium compounds. Drying and heating of the impregnated wood results in the precipitation of insoluble zirconium-copper-borate complexes. Rosin esters, Montan wax, and other resins have been used along with fungicide - e.g., creosote - to anchor the fungicide and retard leaching from the timber.

The recent Rowell process (U.S. Forest Service) utilizes a 20-90 minute 120°C, 150 psi* treatment with propylene or butylene oxide (5 percent triethylamine catalyst) to obtain a rot- and termite-resistant wood. The alkyl oxide undoubtedly reacts chemically with carboxyl and hydroxyl groups in the wood cellulose.

A considerable amount of work has been carried out in the last few years on antifouling slow-leaching organism poisons for ship hulls. Both plant - e.g., sea grass - and animal - e.g., barnacle - organisms (at least 4000-5000 species of plant and animal organisms) can attach themselves to ship bottoms. The principal effective ingredients for these coatings - i.e., tin compounds - are also fungicidal. Alkyl tin methacrylate copolymers appear to be a common active ingredient. Some limited work has also been carried out with the pentachlorophenol methacryloyl chloride reaction product. In all probability this reaction product hydrolyzes slowly, releasing pentachlorophenol.

Some work has been carried out with reacted-on materials for antibacterial cotton fabrics by the U. S. Department of Agriculture. For example, cotton fabric is reacted with phosphorous oxychloride in DMF (dimethyl formamide) at 65-80°C and then treated with potassium thiocyanate at 150°C in DMF.

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* 10^6 Pa

FLAME RETARDANCE

At the present time, flame-retardant timbers are rarely used in U. S. mines. In metal mines such timbers could, if used, probably prevent mine fires of any consequence. In coal mines, flame-retardant timbers could contribute to safety by blocking off a percentage of the (coal) walls.

Impregnation

In ancient times certain salts were deposited beneath the surface of wood to effect a flame-retardant glaze in the event of fire.

The Quartermaster carried out a large amount of work during World War II on flame retardants for cotton. The discovery of great importance resulting from this work was that substances which decompose to phosphoric acid catalyze the formation of char from cellulose. This char is much less flammable than the usual vaporizable decomposition products of burning cellulose or cellulose in the proximity of intense heat. Borate salts, sodium silicate, and ammonium salts are fairly effective flame retardants for wood.

Some mines in Great Britain use timber impregnated with "Fyrprufe", a solution of 89 percent ammonium sulfate, 5 percent ammonium phosphate, 2 percent sodium chromate, and 4 percent sodium fluoride (the chromate and fluoride are probably for fungicidal purposes). Fairly large-scale tests with 2.7 pounds of Fyrprufe solids per cubic foot* of timber indicated that the composition definitely reduces the weight of timber consumed during a fire of less than 20 minutes' duration. Higher air speeds in the tunnel reduce the effectiveness of the flame retardance, but a considerable improvement over the untreated timber can still be shown (fires lasting longer than 20 minutes result in much higher or total timber consumption).

All of these methods show problems in wet environment due to leaching of the soluble salts. Recent work with a phosphoric acid/dicyandiamide impregnation indicates a "nonleachable" retardancy, probably due to cross-linking of the guanyl urea phosphate between cellulose hydroxyl groups. Ferrocene has come into widespread use in polyvinyl chloride compounds to increase char and decrease smoke generation.

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* 43 g/1000 cc

The textile people use (1) reacted-on THPS (tetra kis hydroxy methyl phosphonium chloride) or amino resin coreactants thereof, and (2) APO (tris aziridinyl phosphonium oxide). Some phosphorous amides and N-methylolamide derivatives of phosphines and phosphine oxides also find use. These materials react with the cellulose hydroxyls and are difficult to remove by laundering.

Coatings

Coating materials with a low flame spread rating have been known and used for some time in industry. Flame-resistant coatings may be divided into conventional and intumescent categories.

Conventional polymers and coatings generally fit into a pattern of (1) halogen-containing, usually with phosphorous compounds and antimony oxide (especially 1 mol Sb_2O_3 to 3 mols of halogen) adjuvants; and (2) high phenyl content - especially assisted by aluminum oxide hydrate, nitrogen content, and/or phosphorous compound content.

Smoke and acrid or toxic fumes from the plastic adjacent to the flames is another problem. Generally the halogen compositions have a high acrid and toxic gas generation potential. The so-called "space polymers" - e.g., polyimide and polybenzimidazole - with their high phenyl content, generate a very high char content on exposure to flame, hence have a low smoke and acrid fume potential.

Intumescent coatings require a material capable of generating foam (e.g., nitrogen, ammonia from melamine or ammonium salts, etc.) and a material capable of generating a strong char structure (e.g., pentaerythritol). The foamed char generated by exposure to flame insulates and protects the substrate. Halogen-containing polymers are generally used as the binder. Intumescent coatings tend to leach out their somewhat water-soluble ingredients.

A list of our more productive contacts and sources of information in the wood preservation and fungicide area follows:

American Wood Preservers Association
Forest Products Laboratory
Forest Products Research Society

E. I. du Pont de Nemours

Chevron Chemical Company

Dow Chemical Company

American-Hoechst

Ciba-Geigy

Monsanto

Merck & Company

Alcolac

R. T. Vanderbilt

Tenneco

Mooney Chemicals

M&T Chemicals

Dover Chemical

Sherwin-Williams

U. S. Bureau of Mines

U. S. Department of Agriculture

The Mining Engineer - especially, D. G. Wilde: Fire-Retardant Treatments for Mine Timber (March 1972) 281-290.

The Journal of Paint Technology

Lovelock & Gilbert - Microbial Aspects of the Deterioration of Materials.

Nicholas - Wood Deterioration and Its Prevention by Preservative Treatments - Volumes I and II.

Encyclopedia of Chemical Technology

Encyclopedia of Polymer Science & Technology

The Journal of Fire and Flammability

D'Allelio-Parker: Ablative Plastics

Journal of the Oil Colour Chemical Association - especially C. J. Evans, P. J. Smith: Organotin-Based Anti-Fouling Systems 58 (1975) 160-168.

Chemical & Engineering News - especially page 20 of September 29, 1975; page 18 of April 14, 1975; and page 40 of July 28, 1975.

Willeitner - Fette Seifen Anstrichmittel 76 No. 12 (December 1974) 533-538.

NTIS AD-A020 153. Montemarano: Antifouling Glass-Reinforced Composite Materials (January 1976).

Journal of Coatings Technology. Steele and Drisco: Fungal-Resistant Organotin Resins 48 No. 616 (May 1976) 59-63.

Intern. Polymer Science & Technology. Belokon: Methods for Determining the Fungus Resistance of Plastics 2 No. 1 (1975) p. T/105-6.

Journal of Coatings Technology. Pittman: Chemical Anchoring of Mildewcides in Paint 48 No. 617 (June 1976) 31-37.

Forest Products Journal. Toole: Effect of Decay on Crushing Strength 19 No. 10 (October 1969) 36-37.

Monsanto Chemical Company Special Report No. 6090. Young, et al. Use of a Small Flame Tunnel in the Laboratory Evaluation of Flame Spread Rating. (May 5, 1964).

EXPERIMENTAL WORK

REACTIVE FLAME-RETARDANT POLYMER FILM

Criteria

Our criteria for screening polymers was:

1. Presence of groups capable of reacting with reactive fungicides - e.g., -ØOH, -OH, -NH, -ØNH, $-CO_2H$.
2. Lowest possible likely flammability and smoke and toxic fume generation.
3. Likely ability to penetrate the porous structure of the wood.
4. Likely adhesion to wood.
5. Likely to produce a coating suitable to rough handling before installation.
6. Resistant to moist environment.
7. Commercial availability.

Preliminary Flammability Evaluation

The UL-94 procedure was employed. The bottom portion of the vertical coated wood bar was subjected to 10 seconds' ignition with a Bunsen burner (1 inch flame cone); burning time and flaming drips were noted. After flame-out, the bar was reignited for 10 seconds and the procedure repeated.

Films were ignited in vertical position in a similar manner to the above coated wood bars.

Flammability Screening

Preliminary to making and testing fungicide/polymer reaction products, the flammability of the various polymers under consideration was evaluated in thin film form and as coatings on wood. Polymer solutions were painted on wood, dried, and cured. Also, preliminary work with wood was advisable to determine if polyimides could indeed be used with wood (because of the high bake temperatures required for the polyimides).

Quite frequently films give different flammability results versus the standard 1/16 to 1/8 inch thick solid plastic test bars. Resins were dissolved in solvent - usually N-methyl pyrrolidone - at 20-50 percent solids and films were cast on Teflon. Films were dried at 80°C and cured for 1.5 hours at 200°C in the case of polyimides and Xylok 210. Some work was carried out with dicumyl peroxide in Skybond 700 polyimide to reduce the cure time/temperature, but this work was not successful in effecting a noticeable reduction of cure time. (The use of dicumyl peroxide for this purpose has been reported.) Polyimides and PKHH were used as-received or dissolved and then cast. The other materials were formulated as follows:

- Polyester

100	Hooker Hetron 301L (chlorine-containing polyester)
0.25	Nuodex 6% Co
0.60	Lupersol DDM (MEK peroxide solution)

- Furane

100	Quaker Oats Polymeg (furfuryl alcohol resin 438610)
3.5	Catalyst 458610 (acid)

- Melamine/Formal

10	Monsanto Formvar 12/85
40	Monsanto Melamine 1720 solution
43.5	Toluene/Synasol 60/40
0.4	Toluene sulfonic acid

- Epoxy

100	Dow DER 542 (brominated epoxy)
6.6	TETA

Applied from toluene solution

The films were burned by igniting (10 seconds) the vertical films with a Bunsen burner having a 1 cm flame cone, according to UL procedures. Results (Table 1) were much poorer than expected for most of the "flame-resistant" materials in film form. It was thought that films on wood might be more resistant to the effects of heat and flame since the wood might act as a heat sink, thereby giving results more similar to the standard 1.5 - 3 mm test pieces for polyimide, etc., flammability.

Douglas Fir was cut into 13 x 1.3 x 0.6 cm pieces and oven-dried for 16 hours at 105°C. The fir bars were dipped in the various coatings, oven-dried at 80°C, and cured if necessary. The 200°C cure did not seem to "bother" the wood. Two controls were employed: the plain uncoated wood, and wood which we vacuum pressure impregnated with a 20 percent solution of "Fyrprufe", a formulation used to fire-retard timber in some English mines:

89	Ammonium sulfate
5	Ammonium phosphate
4	Sodium fluoride
2	Sodium chromate

Later in the program wood (after vacuum treatment) was also impregnated for 16 hours with a 1 centipoise catalyzed urea-formaldehyde resin solution and dried-cured for 24 hours at 100°C. The urea-formaldehyde solution was in the following proportions:

53.3	Monsanto 8012 urea-formaldehyde (47 percent solids)
45.5	Water
1.25	Ammonium diacid phosphate predissolved in the water

Weight gain was 9 percent, 2.4 lb/cu ft (39 g/1000 cc).

As shown in Table 1, none of the specimens dripped flaming material.

The UL-94 procedure (for coated wood) appeared to yield much the same results as the film tests reported in Table 1.

The DER 542 epoxy showed excellent flame resistance on wood; but as with the Hetron chlorinated polyester and other halogenated compositions, the fume level is very high during exposure to flame.

The "Fyrprufe" was effective for brief flame exposure. Presumably the active ingredients would leach out eventually in a wet mine, however.

The urea-formaldehyde impregnant was also effective but should be leach-resistant.

Most of the "space polymers" were a disappointment as thin films. Only the Skybonds showed immediate promise. The Skybond 700 is rather brittle, however. An attempt to improve the flexibility of this material by blending with Kerimid caused flammability problems. Blending 5 percent of our chlorophenol-formaldehyde adduct with the Skybond did not appear to injure flammability (Table 1). The Skybond 703 appears to be adequate in flexibility, as received. Skybond 703 was selected as the base polymer for further work.

TABLE 1

Unfilled Resin Flammability Tests
Average Film and Coating Thickness: 0.2 mm

Resin	Nature	Manufacturer	Specimen Type	Burning Time (Sec.)		Fume Level
				First Ignition	Second Ignition	
Skybond 700, 703	Polyimide	Monsanto	Film Coated wood	2 15	5 15	Low
Skybond + trichlorophenol formaldehyde adduct 95/5	-	-	Film Coated wood	2 15	5 20	Low
Rhodeftal 200	Amide-imide	Rhodia	Film Coated wood	10 20	Cont.(1) Cont.	Medium
Kerimid 601	Maleimide	Rhodia	Film Coated wood	30 30	Cont. Cont.	Low
Kerimid + Skybond 50/50, Weight/Weight	Polyimide	-	Film Coated wood	5 2	Cont. Cont.	Low
Polyimide 2080	Polyimide	Upjohn	Film Coated wood	Cont. Cont.	- Cont.	Low
Hetron 301L	Chlorinated Polyester	Hooker	Film Coated wood	15 2	Cont. Cont.	High
DER 542	Brominated Epoxy		Film Coated wood	Cont. 0	- -	High
Xylok 210	Alkyl Ether Phenol	Ciba-Geigy	Film Coated wood	3 - $>$20 3 - $>$2-	Cont. Cont.	Medium
Melamine 1720/Formvar 100/30	Melamine/ Formal	Monsanto	Film	Cont.	-	Medium

(1) Cont. = Continuous

...Continued

Table 1 (Continued - 2)

Resin	Nature	Manufacturer	Specimen Type	Burning Time (Sec.)		Fume Level
				First Ignition	Second Ignition	
Furane Polymeg	Furane	Quaker Oats	Film Coated wood	10 Cont.	Cont. -	High
PKHH	Phenoxy	Union Carbide	Film Coated wood	Cont. Cont.	- -	Medium
"Fyrpruf"	Inorganic Salts	-	Impregnated wood	2	3	Low
Resimine 8012	Urea Formaldehyde	Monsanto	Impregnated wood	0	3	Low
Control	-	-	Uncoated wood	Cont.	-	Medium

Cure Cycle

Concurrent efforts with fungicide and leaching thereof indicated that uncrosslinked soluble material was being leached out of the cast polyimide films. A brief study of leachability of polyimide films versus cure temperature was undertaken (16 hours, Soxhlet, methanol).

The results - as shown in Table 2 - indicate quite high cure temperatures (270°C) are required to eliminate leachability of the polyimide components. The 200°C/2 hr is a reasonable cure cycle, however (reasonably tough film, low residual leachable content). Later work with IR (infrared) heating indicated that high surface temperatures can be achieved without transmitting excessive amounts of heat to the interior.

Several curves of oven heat penetration into coated 9 x 9 cm beams and also IR* heating were prepared - see Figures 1 through 5. Thermocouples measuring 0.25 mm OD were placed in small holes in the sides of the timber to obtain the temperature readings. Generally it is felt that temperatures over 110°C cause undesirable strength loss of wood. Time available at curing temperature before a temperature of 110°C was reached in the interior (2.8 cm) is tabulated - Table 3. Higher oven temperatures or IR enable higher skin temperatures and shorter bake oven cycles than a 200°C oven. Varying 250-300°C oven temperatures or IR heating did not change the available curing time to any extent before heating the interior over 110°C, but higher temperatures enable higher polyimide temperatures.

Some work was undertaken to assess the loss of strength by means of a compressive test. Compressive specimens measuring 1.9 x 1.9 x 4.5 cm were cut along the grain from a fir block measuring 4.5 x 4.5 x 1.9 cm. Quadruplicate specimens were tested by ASTM D-143 type procedures wherein modulus and compressive strength (load at collapse) were measured on an Instron at a 1.3 mm/minute loading rate. The 4.5 x 4.5 cm wood block heated for 1 hour at 150°C and 2 hours (continuous) at 200°C was used as a control. Specimens were preconditioned for 2 days at 50 percent RH. Results are tabulated in Table 4.

* 800 Watt, 110 volt, 45.7 cm hot bar Chromalox heater, 7.62 cm above surface.

TABLE 2

Extraction Data on Cured Polymers

Experiment 4507-A

Polymer	Cure: 2 Hr at 150°C Plus	Percent Weight Loss in Methanol, 16 Hours
Skybond 700	200°C, 1 hour	9.9
Skybond 702	200°C, 1 hour	(1)
Skybond 703	200°C, 1 hour	13.1
Skybond 703	200°C, 2 hours	6.7
Skybond 703 precipitated with water, redissolved	200°C, 1 hour	4.1
Skybond 703	200°C, 1 hour, plus 3 hours at 270°C	0.0
Skybond 703 precipitated with water	200°C, 1 hour, plus 3 hours at 270°C	0.0
Xylok 210	200°C, 2 hours	0.0

(1) Too brittle to handle

TABLE 3

Effect of Heat Source/Temperature on External and Internal Heating Rate

Oven Temp. (^{o}C)	Available Time at Curing Temperature (min.) (a)	Total Oven Time to Reach $110^{o}C$ at Position (2) (min.)	Maximum Skin Temp. Position (3) (^{o}C)
200	8	36	176
250	22	30	220
265	23	32	228
300	20	25	240
IR	21	30 (b)	300

(a) Based on time available at Skin Temperature over $172^{o}C$, Position (3), before Position (2) thermocouple reaches $110^{o}C$.

(b) Heat removed at 23 minutes.

TABLE 4

Effect of Temperature on Strength

Experiment Number	Wood Treatment	Av. Modulus $(N/m^2) \times 10^{-6}$	Compressive Strength $(N/m^2) \times 10^{-6}$, Average/Range
4539-12	None - as rec'd	5343	43.36/41.9 - 44.7
4539-14	Heated at 200°C	6418	50.26/48.4 - 53.1

The heat cycle did not appear to have any obvious effect on strength. The data would seem to indicate that the 2 days at 50 percent RH was insufficient to restore full moisture (harder block). Other tests such as flex strength should be carried out, as it does not seem possible that some detrimental effect would not accrue to such a high bake temperature.

Some work was also carried out with IR baking effects. The IR heater utilized for Figure 5 caused a darker center strip 5.1 cm wide immediately under the heating bar. A "Luminator" LH-768, 1600 Watt, 220 volt, IR glass rod heater was positioned 9 cm (heating bar to surface) over a coated 9 x 9 cm beam. Position (2) (2.8 cm deep) reached 110°C at 34 minutes. Position (3) (skin) reached 284°C; and Position (1) reached 78°C. At 45 minutes (3) reached 300°C and (2) reached 125°C. The coating darkened uniformly, indicating that the coating did not overheat in one area with this IR fixture.

In another experiment the top of a 9 x 9 cm cross-section beam was painted black (dispersed carbon pigment), and polyimide baked at 150°C on glass was peeled off and taped onto the 9 x 9 cm beam. The film was baked for 52 minutes, achieving a skin temperature of 272°C. The interior at 2.8 cm was 125°C. The polyimide film was extracted for 3 days in boiling methanol (Soxhlet) and redried. Weight loss was 0.8 percent (see also Table 2).

Another beam was topcoated and baked under the IR heater, coated on the opposite side and rebaked, then cooled. The beam was then cut into small portions measuring 1.3 x 1.3 x 5 cm and tested for compression properties. The results are recorded in Table 5.

The block was then sawed up as follows:

2.5 mm	Coating plus wood - discarded
1.3 cm	Row A, closest to IR - brownish on top side
	Row B, intermediate row
	Row C (middle of block)
	Row D, intermediate row
	Row E, closest to IR, brownish on IR side
2.5 mm	Coating plus wood - discarded

Compressive strength, ASTM D-143 procedures, was evaluated for each row, along with raw wood control pieces cut from an adjacent beam area.

TABLE 5

Effect of IR Cure on Beam Strength/Modulus

Section	Average Modulus $(N/m^2) \times 10^{-6}$	Average Compressive Strength $(N/m^2) \times 10^{-6}$
Control, Unheated		
Row A/E (outer)	3509	41.64
Row B/D (intermediate)	3295	49.52
Row C (center)	2800	56.53
Heated Beam		
Row A/E (outer)	3447	56.12
Row B/D (intermediate)	3654	60.67
Row C (center)	3475	59.25

Thus it would appear by this test that no harm came to the wood at any substantial depth as a result of the IR cure.

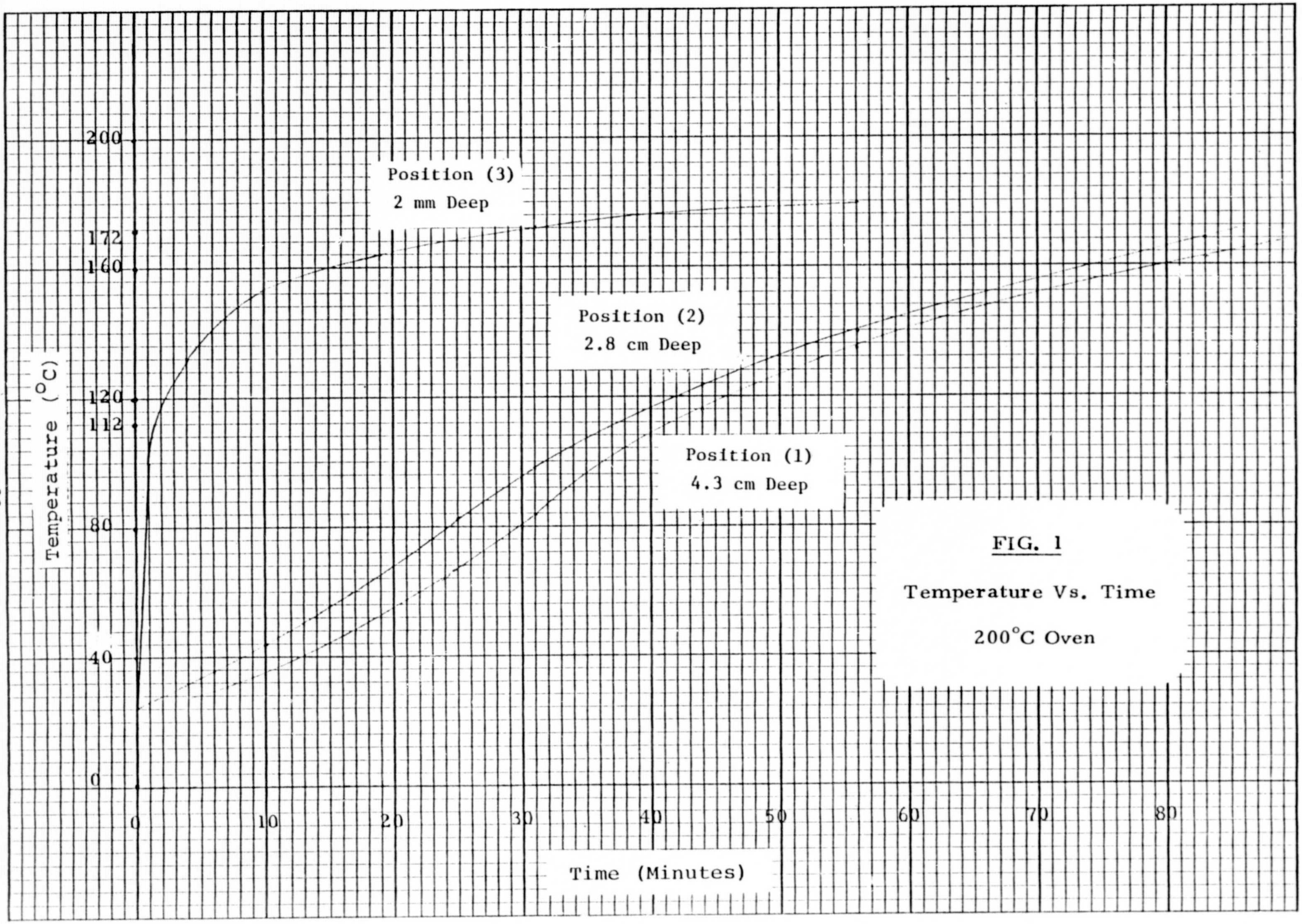


FIG. 1

Temperature Vs. Time

200°C Oven

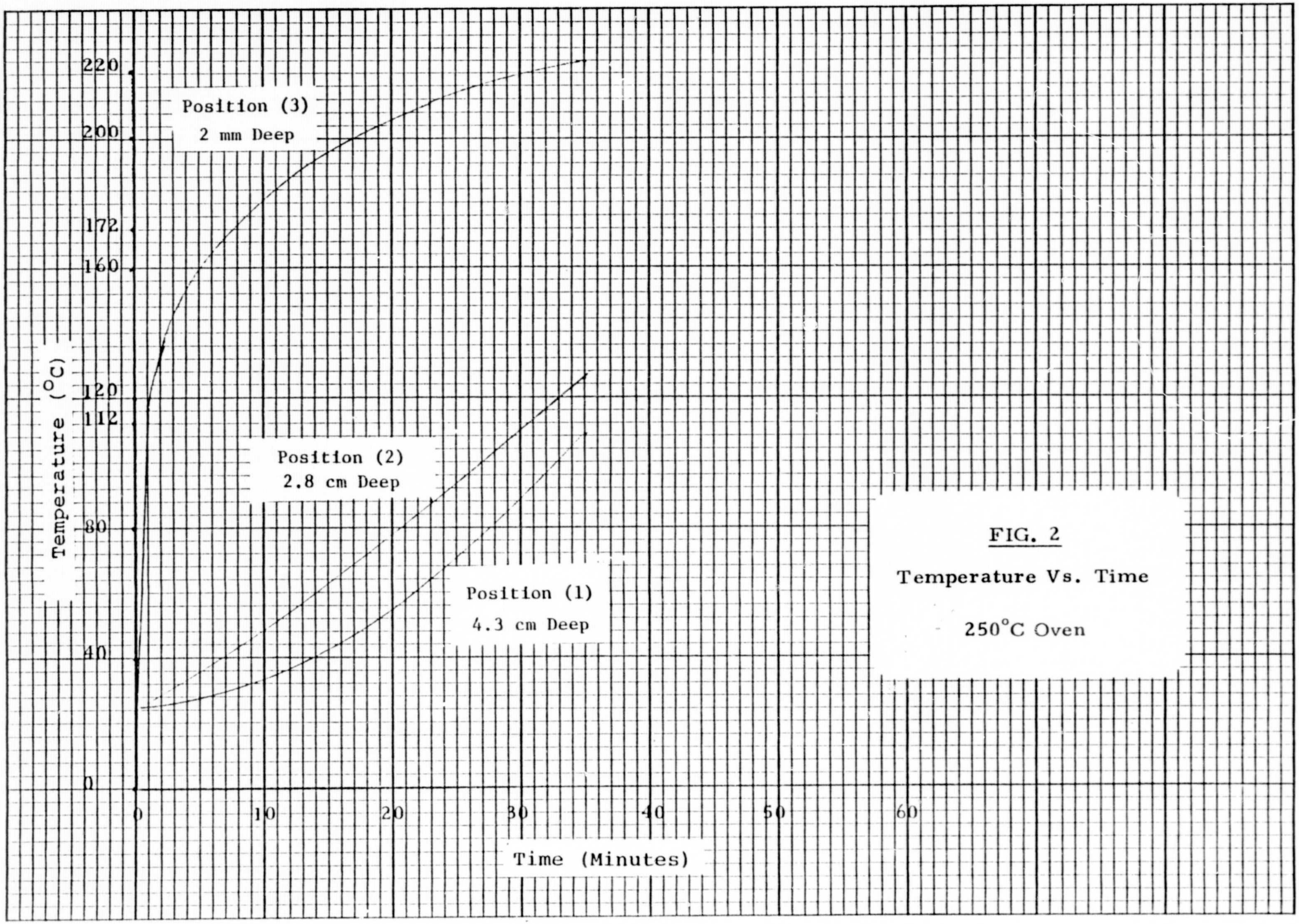


FIG. 2

Temperature Vs. Time

250°C Oven

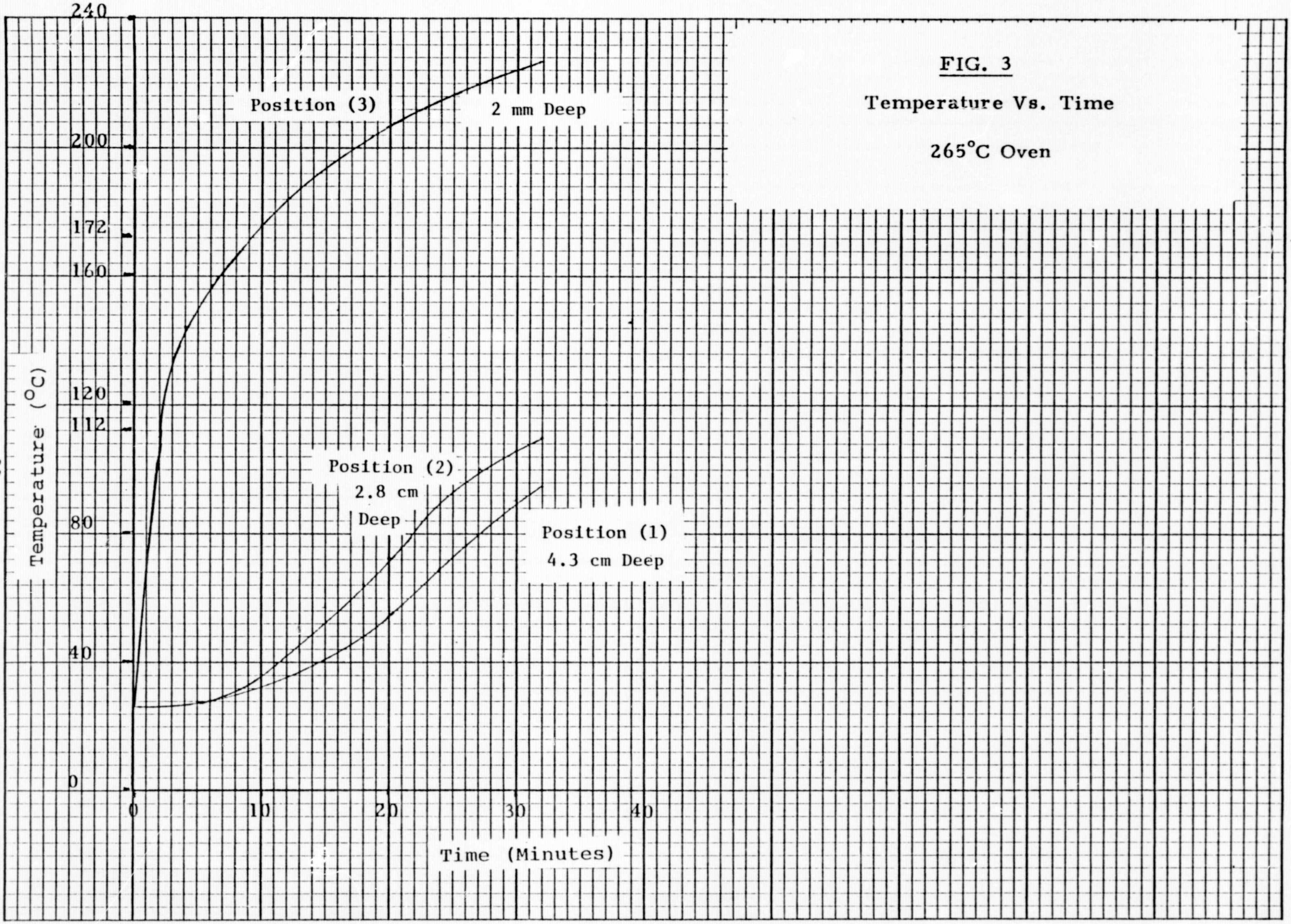


FIG. 3

Temperature Vs. Time

265°C Oven

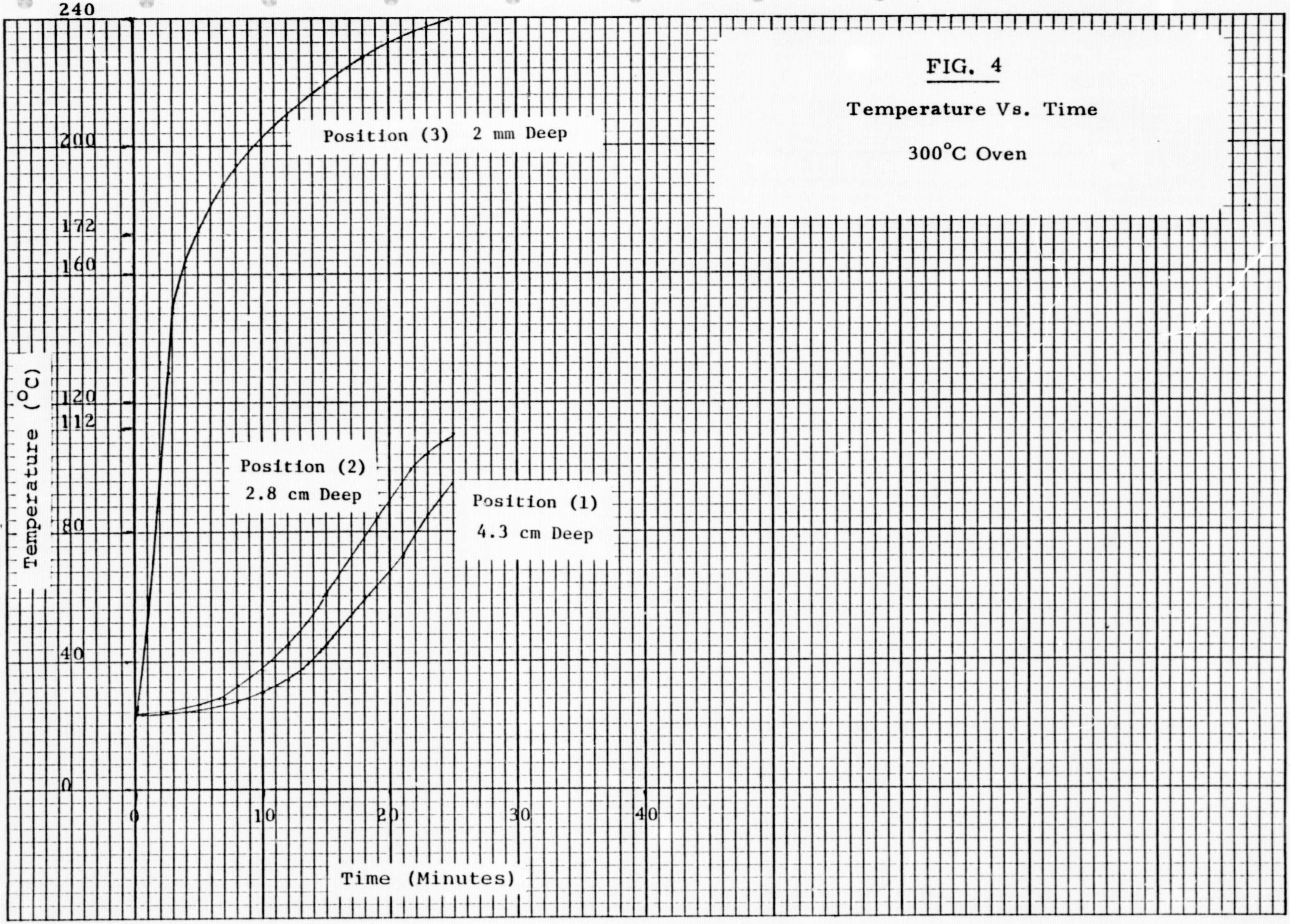


FIG. 4

Temperature Vs. Time

300°C Oven

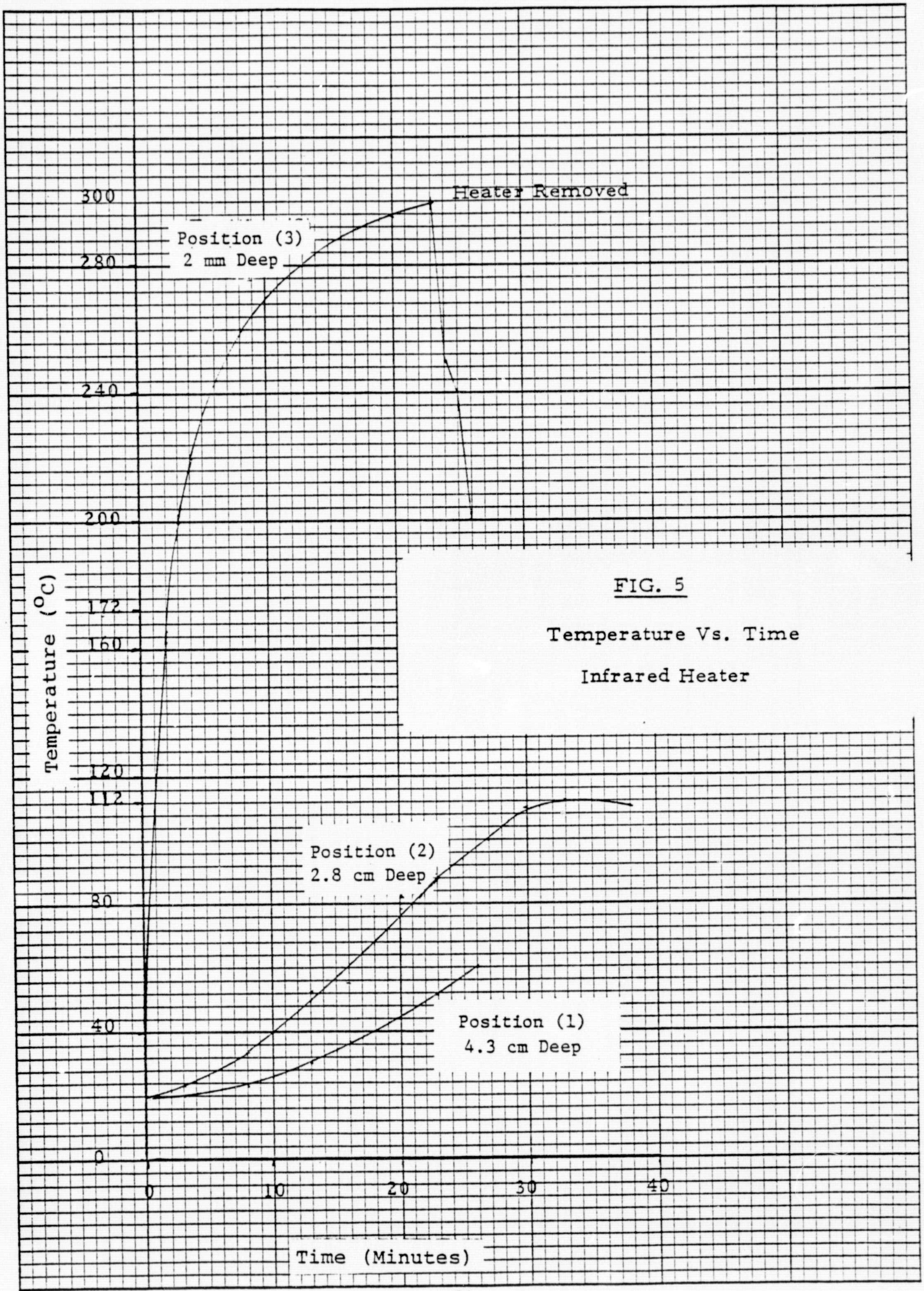


FIG. 5

Temperature Vs. Time

Infrared Heater

Bubble Entrapment

The polyimide, when painted on dry wood and baked, gives a foamed type of surface. A prebake of one hour at 100-120°C was helpful but was not the answer to the problem. Bubbles showed up even at these low temperatures.

Baking films on glass gave the same problem, so the wood was not the cause. Apparently the polyimide cures on the surface and the skin is quite impermeable. As further evaporation of solvent takes place and water evolves from the cure mechanism, the coating forms bubbles and large blisters.

The following foam release aids and solvents were added to 10 parts of Monsanto Skybond 703 and the solution cast to give 0.1-0.13 mm dry films. Promising films were additionally cured for 2 hours at 200°C, but results were similar to the 150°C results.

TABLE 6

Additives to Prevent Bubbles

Experiment Number	Additive	Parts Additive Per 10 Parts Skybond Soln.	Comments, Bubble Content: 1 Hour At: 110°C	150°C
4517-1	Dow Corning DC-6 Silicone	0.1	Many (small)	Increased (hazy coating)
4517-2	Dow Corning DC-200 Silicone	0.01	Some	Increased + BB (big blisters)
4517-3	Monsanto Moda-flow	0.1	None	Many (small); hazy coating
4517-4	Butanol	1.0	Few	Increased in size + BB
4517-5	Xylene	1.0	Some	Many + BB
4517-6	Cyclohexanone	1.0	None	3
4517-7	MIBK	1.0	Some; large	Many + BB
4517-8	Ethyl cellosolve	1.0	None	2 only
4517-9	Cellosolve acetate	1.0	Few	Some large + BB
4517-10	Water	1.0	Few	Many + BB

...Continued

Table 6 (Continued - 2)

Experiment Number	Additive	Parts Additive Per 10 Parts Skybond Soln.	Comments, Bubble Content 1 Hour At: 110°C	150°C
4517-11	Ethylene glycol	1.0	Few	Many + BB
4517-12	Propylene glycol	1.0	Some	Many + BB
4517-13	None (control)	-	Some	Many + BB
4522-14	Diacetone alcohol	1.0	Few	Few
4522-15	Ethyl carbitol	1.0	Some	Some
4522-16	Butyl carbitol	1.0	None	9
4522-17	Butyl cellosolve	1.0	None	None
4523-18	Methyl cellosolve	1.0	None	None
4523-19	Isophorone	1.0	None	None
4523-20	Ethyl cellosolve Modaflow	1.0 0.1	Some	Some;cloudy
4523-21	Dipropylene glycol	1.0	None	1 only
4524-22	Diethylene glycol	1.0	None	25 - on edge
4526-25	Butyl cellosolve	2.0	None	4
4526-26	Butyl cellosolve MIBK	2.0 1.0	One	Some
4526-27	Butyl cellosolve Butyl acetate	2.0 1.0	Few	Some
4527-28	Butyl cellosolve Isopropanol	2.0 1.0	Few	Few

It would appear that butyl cellosolve is the best additive, at 1-2 parts per 10 parts Skybond (-17, -25). Use of low boilers to help "set" the formulation more readily causes some problem (-26, -27, -28). Isopropanol is the best diluent. The butyl cellosolve formulations on dried wood do yield some bubbles, however - especially along the porous summer growth grain.

Thixotrope

Three thixotropic aids (0.3 grams) were ground into 10 Skybond in a mortar and pestle and one part butyl cellosolve was added. The formulations were painted on wood and baked for 1 hour at 120°C, 1 hour at 150°C, and 2 hours at 200°C, with the following observations:

Additive	Bubbles	Painting Smoothness	Final Coating Smoothness
Cabot Cab-O-Sil EH-5	Few	Okay	Okay
NL Bentone 27	Very few	Okay	Okay
Carbide Asbestos RG-294	Few	Best thixotrope	Okay

The Bentone tends to settle out on standing. The Carbide predispersed asbestos is probably the best thixotrope in this polyimide system, but use of asbestos in the formulation is probably undesirable. The Cab-O-Sil does a reasonable job, and a large masterbatch of Skybond/Cab-O-Sil was prepared using 5 minutes of high-speed stirring with a high-speed Cowles-type agitator.

REACTIVE FUNGICIDE

Criteria

The potentially reactive fungicides considered are tabulated in Table 7, Potentially Suitable Fungicides. Eventual selection of the polyimide coating affected fungicide selection. Some fungicides would not likely be stable at the high polyimide bake temperature - e.g., azo materials, isocyanate reaction products. Some fungicides would not likely react with polyimide constituents - e.g., the polyimide prepolymer offers reactive amine, acid, and benzene ring substituents. Other reactions might be too permanent - e.g., HOØCl + NH_2R ⟶ HOØNHR - and would likely not revert eventually to free leachable fungicide. The reactions of the fungicides used in the program pertinent to polyimide are marked with the superscript "7".

TABLE 7

Potentially Suitable Fungicides

Fungicide	Manufacturer	Type	Reactive With	Suitable Resin System (a)
Pentachlorophenol	Dow	Phenolic	Isocyanate; acid;[7] amine;[7] acrylic chloride	1,2,3,6,7,8
2,4,5-trichlorophenol	Dow	Phenolic	Ditto + ; formaldehyde[7]	1,2,6,7,8
Tetrachloro bisphenol-A	Dover	Phenolic	Isocyanate; acid; formaldehyde; amine	1,2,6,7,8
Hexyl resorcinol	American-Hoechst	Phenolic	Isocyanate; acid; formaldehyde	1,2,6,7,8
Salicyl anilide	Pfister	Phenolic	Isocyanate; formaldehyde; epichlorhydrin; acrylyl chloride	1,2,3,5,6,7,8
Butyl-p-hydroxybenzoate	Malinckrodt	Benzoate	Isocyanate; acid; amine; formaldehyde	1,2,6,7,8
Propyl-p-hydroxybenzoate	Malinckrodt	Benzoate	Isocyanate; acid;[7] amine;[7] formaldehyde[7]	1,2,6,7,8
Hexyl-p-hydroxybenzoate	Malinckrodt	Benzoate	Isocyanate; acid; amine; formaldehyde	1,2,6,7,8

(a) Resin systems: 1. Phenoxy 2. Furane 3. Polyester 4. Polycarbonate 5. Epoxy 6. Polyimide 7. Polyamide-imide 8. Bismaleimide

...Continued

Table 7 (Continued - 2)

Fungicide	Manufacturer	Type	Reactive With	Suitable Resin System
Tributyl tin acrylate	Polysciences	Organometallic	Vinyl groups	2,3
Tributyl tin methacrylate	Polysciences	Organometallic	Vinyl groups	2,3
Chromium methacrylate	Polysciences	Organometallic	Vinyl groups	2,3
Trimethylamino-1-chloro-2-hydroxypropyl methacrylate	Alcolac	Quarternary	Vinyl groups	2,3
Dimethyl sulfate/dimethyl-amino ethyl methacrylate	Alcolac	Quarternary	Vinyl groups	2,3
Chloromethyl dimethylamino ethyl methacrylate	Alcolac	Quarternary	Vinyl groups	2,3
2-(4-thiazolyl) benzimid-azole (TK-100)	Merck	Thiazole	Phosphonitrilic chloride; epichlorhydrin; acrylyl chloride; acid[7]	1,2,3,5,6,7,8
Hydroxymethoxy methyl azo dioxabicyclo octane	Tenneco	Azo	Isocyanate; phosphoni-trilic chloride	1,2,5,6,7,8
Copper 8-quinolate	Tenneco	Metal complex	Phosphonitrilic chloride; epichlorhydrin; acrylyl chloride	1,2,3,5,6,7,8
Copper 8-hydroxy quinolate	Tenneco	Metal complex	Isocyanate; phosphoni-trilic chloride; epichlor-hydrin	1,2,5,6,7,8
Dehydroacetic acid	Eastman	-	Amino groups	6,7,8

...Continued

Table 7 (Continued - 3)

Fungicide	Manufacturer	Type	Reactive With	Suitable Resin System
2,4-dinitrophenol	American-Hoechst	Nitrophenol	Formaldehyde; isocyanate	1,2,6,7,8
2,4-dinitroaniline	American-Hoechst	Nitrophenol	Epichlorhydrin; phosphonitrilic chloride; acrylyl chloride	1,2,3,5,6.,7,8
2,6-dibromo-p-nitroaniline	Salsbury	Nitrophenol	Epichlorohydrin; phosphonitrilic chloride; acrylyl chloride	1,2,3,5,6,7,8
3,4,5-tribromo salicyl ahalide	Pfister	Phenolic	Isocyanate; acid; amine; formaldehyde; epichlorhydrin; acrylyl chloride	1,2,3,5,6,7,8

Preparation of Blocks for
Fungus Resistance Testing

Blocks measuring 4.5 x 4.5 x 1.9 cm were cut from a fir "two-by-four" beam. Knot-containing blocks were discarded. The blocks were dried at 110°C overnight. Impregnation, where utilized, took place next, and the blocks were redried.

The coating was painted on and set by heating for 1 hour at 120°C and 1 hour at 150°C. Any (brittle) bubbles were removed by rolling the surface. A second coat was applied and dried/cured for: 1 hour at 120°C, 1 hour at 150°C, and 2 hours at 200°C. A slot 5 mm deep was sawed into each block after coating.

Impregnation -

- "Fyrprufe" (4545-1, -1A)

The following composition was dissolved in water:

89	$(NH_4)_2SO_4$
5	$(NH_4)_2HPO_4$
2	$Na_2Cr_2O_4$
4	NaF
400	Water

Four wood blocks, dried at 110°C, were evacuated in a bell jar (aspirator) for 1/2 hour*, the Fyrprufe solution was admitted to cover the blocks, then the bell jar was repressurized to 1 atmosphere and the blocks allowed to soak for 16 hours at room temperature (61 grams of solution absorbed per 100 grams of wood). The blocks were redried at 110°C. Previous experience indicated that such impregnated blocks were very flame retardant(Table 1).

- Polyimide (4544-1)

Dry wood blocks were impregnated with the following solution:

50	Monsanto Skybond 703 (65 percent solids)
1.63	Dow Dowicide 2, trichlorophenol
40	Isopropanol
0.6	Acetone

* Similar to ASTM D-1413 procedures

Impregnation was carried out by evacuating the wood blocks in a chamber for 1/2 hour and admitting the above solution to cover the blocks, then repressurizing to 1 atmosphere for 1/2 hour. Weight gain after curing was 11.4 grams per 100 grams of wood (3 lb/cu ft; 49 g/1000 cc) (including allowance for a 4 percent weight loss of plain wood exposed to the same curing conditions.

Metal Complex Fungicide Coatings -

Report AD-A020 153, NTIS; Montemarano, et al - "Antifouling Glass-Reinforced Composite Materials" - indicates that tributyl tin compounds reacted in with polyester or epoxy polymers have been effective against sea water fouling organisms for up to thirty-one months in on-going tests. These results would indicate that many reacted-in compounds do leach, but at a slower rate than simple additives.

- Copper (4540-1)

The following was charged to an open beaker fitted with stirrer and thermometer:

	Weight	Solids
Monsanto Skybond 703	30	19.5
Fischer cupric acetate hydrate	1.27	(0.41 Cu)

The charge was heated at 90°C for 2.5 hours until the greenish particles of copper acetate disappeared. Presumably the copper ion reacts with the available polyimide prepolymer carboxyl content and gives off the acetic content of the copper acetate. Butyl cellosolve, 6 parts, was added and the solution cooled. The solution was painted on wood blocks (see 4539-10 in Table 8*) and cured. Films were also cured at 200°C and leached with boiling methanol and water for 72 hours (Soxhlet). The films were analyzed for copper content (Galbraith). The results were:

% Cu	
1.50	Original (theoretical, 2.0%)
1.34	Leached, methanol
1.36	Leached, water

* Pg 37

Very little of the copper is apparently readily leachable.

A previous experiment (4538-1) utilized cupric carbonate powder instead of copper acetate, but the carbonate was slow to react. After 4 hours at 90°C and 1 hour at 120°C, the polyimide was greatly increased in viscosity but the copper carbonate particles were still evident (microscope).

- Tin (4528-30)

Skybond 703 (30 grams) was reacted with 1 gram bis(tri-n-butyl tin)oxide at 90°C for 1 hour (reported July 27). Cast, cured films were analyzed for tin content (Galbraith) with the following results:

% Sn	
1.9	Original (theoretical, 2.0%)
2.0	Leached, methanol
2.1	Leached, water

The analysis is probably ±0.1 percent, which would mean substantially no tin compound was leached in 72 hours.

- Tin Polymer (4536-1)

The following charge was polymerized for 16 hours at 60°C in a nitrogen filled, sealed bottle (4536-1):

1	Tin acrylate (32.8% tin - Polysciences)
1	Diacetone acrylamide (Lubrizol)
0.02	Vazo 52 (DuPont)
20	Toluene (reagent)

The tin copolymer was precipitated in hexane, washed with hot hexane, and dried. Polymer (melting point, 80°C) was soluble in methanol; insoluble in water. Analysis: 7.45 percent tin.

The coating was prepared as follows (4536-1A):

	Weight	Solids
Monsanto Skybond 703	10	6.5
4536-1 (7.45% Sn)	0.33	0.33
Butyl cellosolve	2	-

The coating was cast as a film and cured, then leached (72 hours, Soxhlet) and analyzed for tin content (theoretical, 0.38%). The results were:

% Sn	
0.39	Original
0.40	Leached, methanol
0.39	Leached, water

Again the film was resistant to loss of tin by leaching. The amount of tin present in the film is probably too low, however.

The diacetone acrylaminde was used as a copolymer to enable ready solubility in polar solvents and the polar polyimide, and also to offer sites for interreaction with the polyimide.

The system is more complex and more expensive than the preceding 4528-30 and was not pursued further at this time.

Organic Fungicides -

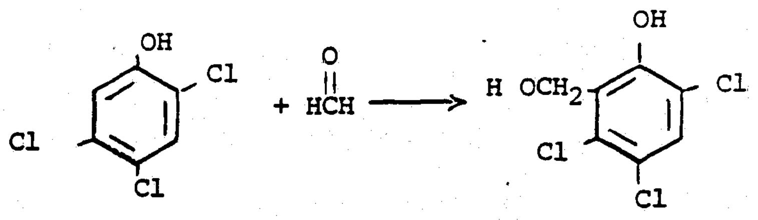
- Formation of Reactive Fungicide Intermediate

Two unavailable reactive organic fungicide intermediates were synthesized early in the program.

1. Reaction with Aldehyde (A4501)

An amount of 0.1 moles of 2,4,5-trichlorophenol (Dowicide 2) was dissolved in 150 grams of dioxane (analytical grade). The temperature was raised to 80°C with rapid stirring and a solution containing 0.3 moles (stoichiometric excess) of formaldehyde was added over 1/2 hour. Reaction was continued for 2 hours and the product isolated in a rotary vacuum evaporator. Characterization was conducted by thin-layer chromatography (TLC) using acetic acid/chloroform (1:9) as the developing solvent and ferric chloride as the visualization reagent. The mixture appeared to be almost entirely trichlorophenol methylol adduct (two possible isomers) with small quantities of unreacted and disubstituted material. Assay by UV techniques was 52 percent chlorophenol.

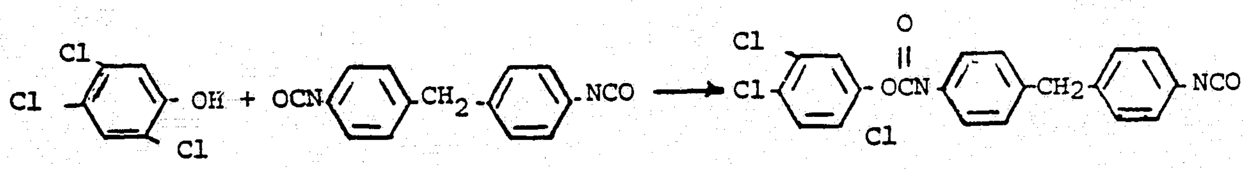
Chemically, the formulation was as follows:



2. Reaction with Isocyanate

An amount of 0.1 moles of methylene diphenyl diisocyanate ("MDI" - Upjohn 143 L) was dissolved in 100 ml anhydrous ethyl acetate under a nitrogen atmosphere and heated to 40°C. A solution of 2,4,5-trichlorophenol (0.1 moles) in ethyl acetate was then added over the course of 3 hours with rapid stirring. The resulting product was isolated in a rotary vacuum evaporator as a viscous clear brown oil. Thin-layer chromatography was performed using acetic acid/chloroform (1:9) followed by visualization with iodine vapor. The presence of one large spot indicated that only one compound was predominant.

Infrared spectroscopy showed the presence of chloride substitution, residual active isocyanate, and other bands common to both reactants. The product was stored in a cold room under nitrogen. Its chemical formulation follows:



The isocyanate intermediate was not felt to be suitable for the later-developed polyimide coating and was not used in the program. (The isocyanate-phenol adduct decomposes at 150-200°C; urethane groups are not stable for prolonged periods of time at 200°C or even for short periods if the polyimide is cured at a temperature over 200°C.)

• Formulation

The fungicide was weighed into the polyimide:

	Weight	Solids
Monsanto Skybond 703	100.0	65.0
Cabot Cab-O-Sil EH-5	3.0	3.0
Fungicide (Table 8)	3.3	3.3
Butyl Cellosolve	20.0	---

The solution was painted on the wood - two coats. The first coat was set by heating for 1 hour at 120°C and 1 hour at 150°C. The second coat was set by heating for 1 hour at 120°C, 1 hour at 150°C, and cured by heating for 2 hours at 200°C. Following the coating process, a slot 5 mm deep was sawed into each block with the purpose of permitting the fungus and any leachable fungicide to "get at" the uncoated wood.

The formulations submitted for fungus testing are presented in Table 8. The potential reaction modes of the fungicide with polymer 7 polyimides were tabulated in Table 7, page 28. Essentially, for example, the propyl hydroxy benzoate has a reactive phenolic-OH capable of reacting with the polyimide prepolymer anhydride, acid, and amine content. Chlorophenol could react through the phenolic hydroxyl, or the aromatic chlorines could react with the aromatic amine content of the polyimide prepolymer. The formaldehyde/chlorophenol adduct could react with polyimide prepolymer acid, amine, or aromatic ring content. The benzimidazole (4539-4, -6) has a reactive -NH which could presumably react with a carboxyl to form an amide and could possibly react with an aromatic amine in the polyimide -- e.g., $RNH + NH_2\emptyset \longrightarrow RN\emptyset + NH_3$.

The benzimidazole was screened at a lower concentration (4539-6) because it is an expensive material.

• Leach Testing

Work was also undertaken to determine if cast films would leach out fungicide. Films cast on Teflon were cured for 1 hour at 120°C, and 2 hours at 200°C. Leaching was carried out in a Soxhlet with water or methanol. Since the film itself loses some material with a 2-hour, 200°C cure, a method was developed to assay the leached-out material in the Soxhlet still pot.

TABLE 8

Formulations for Fungus Resistance Testing

Ingredients	4539-											4545-		4544-
	1	2	3	4	6	5	7	8	10	11	12(1)	1	1A	1
Skybond polyimide solution with Cab-O-Sil (3%)	100	100	100	100	100	100	100	100	-	-	-	-	100	100
Dowicide 2 (trichlorophenol)	3.3	-	-	-	-	-	-	-	-	-	-	-	-	3.3
A-4501, Dowicide 2/formaldehyde adduct	-	6.7	-	-	-	-	-	-	-	-	-	-	6.7	-
Propyl-p-hydroxy benzoate	-	-	3.3	-	-	-	-	-	-	-	-	-	-	-
Metasol TK-100/benzimidazole	-	-	-	3.3	1.7	-	-	-	-	-	-	-	-	-
Dowicide EC-7 (pentachlorophenol)	-	-	-	-	-	3.3	-	-	-	-	-	-	-	-
Ziram (zinc dimethyl dithiocarbamate)	-	-	-	-	-	-	3.3	-	-	-	-	-	-	-
4501-1 (copper-reacted)	-	-	-	-	-	-	-	-	100	-	-	-	-	-
4528-30 (tin-reacted)	-	-	-	-	-	-	-	-	-	100	-	-	-	-
Butyl cellosolve	20	20	20	20	20	20	20	20	20	20	-	-	20	20
Wood pretreatment	-	-	-	-	-	-	-	-	-	-	-	(2)	(2)	(3)

(1) As-received wood

(2) Impregnated with "Fyrprufe"

(3) Impregnated and then painted with 4539-1

1. Fungicide Assay

The (aromatic) fungicide to be assayed is made up in three concentrations in solvent of interest, within the range of the spectrometer. A Bausch & Lomb Spectronic 505 (2000-5000 Å) is utilized for this work. Peak height is measured in centimeters above the plain solvent curve and peak height is plotted versus concentration of fungicide.

The leachate is assayed by reading peak height differential versus the solvent and picking the concentration value off of the peak height versus concentration curve. Since the method is very sensitive, sometimes it is necessary to dilute the leachate 10 or 20 to 1. The formulation is:

Leached fungicide = assay/cc x grams of fluid ÷ density of fluid

Aromatic material leaches out of the 200°C-cured polyimide, but fortunately it absorbs in the range of 2100 Å and does not interfere with the fungicide peaks evaluated to date. Thus:

Fungicide	Peak (Å)
TK-100	2970
Dowicide 2	2920
4501	2920
Propyl hydroxybenzoate	2560
(Imide film materials)	2100

2. Leaching

Cured Formulation 4513-1 Skybond solids/trichlorophenol, 100/5 (cf 1 gram film) was extracted (Soxhlet) for 72 hours in methanol. The leached material was assayed daily:

Leaching Time (hr)	Leached Fungicide Materials (g)	Total Fungicide Content Leached (%)
24	0.0223	35.0
48	0.013	55.2
72	0.0049	63.4

Apparently at least three days are required to substantially leach the material, and it is not certain but that ester interchange or hydrolysis may enable a continuous supply of leachable material - thereby giving an artificially high leachable content. Additional films were cast, cured at 120°C 150°C, and 2 hours at 200°C, and leached for three days in a Soxhlet with methanol or water. Results are presented in Table 9.

The data would indicate that the fungicide does not leach readily from the cured polyimide, particularly in hot water. The data also indicate that the trichlorophenol/formaldehyde adduct (-2) was less leachable in alcohol than was the unreacted chlorophenol (-1). The TK-100 (-4) was very resistant to methanol leaching. Possibly the material formed an amide reaction prod- with the acid in the Skybond, and this amide would be expected to have a much greater resistance to hydrolysis than the phenolic ester compounds (-1 and -3).

We are not certain at this point whether the discrepancy in leaching - water versus alcohol - is the result of: (1) hydrolysis of bonds; (2) ester interchange of the alcohol leachant interacting with the polyimide/fungicide reaction product; (3) the fact that water just does not penetrate the polyimide as well; or (4) very low fungicide solubility in water.

TABLE 9

Leach Data, Methanol and Water, on Four Cured Skybond 703/Fungicide Films

Experiment 4513-	Fungicide -	phr	Leached Fungicide (%)	
			Methanol	Water
1	Dowicide 2 (trichlorophenol)	5.0	63.4	2.9
2	Trichlorophenol-formaldehyde	5.7	31.3	2.4
3	Propyl p-hydroxy benzoate	5.0	88.3	0.62
4	Merck TK-100 NH-containing benzimidazole	5.0	16.2	4.3

Fungus Testing

A combined ASTM G-21 and D-1413/D-2017 test procedure was utilized. The G-21 procedure is commonly employed for coatings. The coated object is incubated with the fungus mixture, or sometimes a single fungus species, and the surface is visually rated for extent of fungus growth. The D-1413/D-2017 procedures involve incubating feeder blocks with the wood-attacking fungus for three weeks, placing the weighed block to be tested on the feeder blocks, and allowing several weeks of exposure to the fungus. The blocks are then scrub-washed, treated with a mercurial, dried, and reweighed.

In our case, the fir blocks were dried, sealed, shipped to our Bioresearch division, weighed, and subjected to 10 weeks of contact with the following fungi growing on feeder blocks:

Especially for polymer attack - ASTM G-21

- Aspergillus niger
- Penicillium funiculosum
- Chaetonium globosum
- Trichoderma Sp
- Pullularia pullulans

Especially for hard and soft wood attack - ASTM D-1413/D-2017

- L. Trabea Pers. ex. Fr.
- Polyporus versicolor
- Poria placenta
- Lentinus lepideus

The condition of the blocks was visually examined at 3 and 6 weeks with respect to growth on the surfaces ("0" none, "10" very extensive). The blocks were washed, redried, and reweighed at 10 weeks. Results are presented in Table 10.

TABLE 10

Extent of Fungus Growth

Experiment Number	Fungicide in Polyimide	Wood Impregnant	Rating (6 Wks)	Wood Weight Loss - Grams (10 Weeks)	
				Series I	Series II
4539-3	Propyl p-hydroxy benzoate	-	0,1	0.84;0.70	-
4539-10	Copper	-	0,1	0.76;0.81	-
4539-7	Vanderbilt Ziram	-	1,1	-	0.47;0.53
4539-5	Pentachlorophenol	-	1,1 (a)	0.67;0.73	-
4539-8	None - Control	-	1,1	0.70;0.81	-
4539-11	Tin	-	0,2	0.69;0.73	-
4539-6	(Low) benzimidazole content (Merck TK-100)	-	0,2	-	0.43;0.49
4544-1	Trichlorophenol	Trichlorophenol + Skybond	1,3	0.80;0.83	-
4539-1	Trichlorophenol	-	1,3	0.86;0.85	-
4539-4	Benzimidazole TK-100	-	1,2	-	0.38;0.39
4539-2	Trichlorophenol-formaldehyde	-	2,2	0.73;0.78	-
4545-1	(b)	Fyreprufe	2,2 (a)	1.69;1.86	-
4545-1A	Trichlorophenol-formaldehyde	Fyreprufe	3,3 (a)	1.17;1.17	-
4543-14	(b) (Wood baked at 200^{o}C)	-	7,7	0.71;0.70	-
4539-12	(b) Control (as-received wood)	-	10,10	1.09;1.17	-

(a) Very luxuriant fungus growth in jar (b) No coating

Results thus indicate that:

- The polyimide itself (4539-8) appears to be fungus resistant (in addition to its many other desirable properties).
- The propyl hydroxybenzoate appears to be a slight improvement (4539-3).
- The copper-containing coating (4539-10) shows some improvement over the control (-8).
- The pentachlorophenol (4539-5) and Ziram (4539-7) were not visually rated any better than the control.
- The trichlorophenol (4539-1) appeared somewhat less effective than the control (-8) or pentachlorophenol (-5). The trichlorophenol impregnated into the wood along with the polyimide coating (4544-1) did not offer any improvement over plain coating (4539-1). The trichlorophenol/formaldehyde adduct (-2) was less effective than the 4539-1 plain trichlorophenol.

  Trichlorophenol/formaldehyde over wood containing the Fyrprufe treatment (4545-1A) was still less effective. Apparently the Fyrprufe phosphate sweats through pinholes in the coating and feeds the fungus growth. Note the higher weight loss versus plain wood block baked at a similar temperature (4543-14).
- The Fyrprufe-impregnated, uncoated block (4545-1) was an improvement over the control (-12). Although the 4545-1 leaching rate or weight loss is high, as expected, probably some of the chromate and fluoride also leach out to poison the fungi on the wood surface. Apparently both of the coated Fyrprufes fed phosphate (?) to the culture in the bottle. See Footnote (a) on Table 10.
- None of the fungicide plus polyimide formulations could be considered an outright failure.

The wood weight loss data did not do as much for us as hoped. The initial weight of the wood blocks was 15-16 grams. The weight loss of wood baked at 200°C (-14) was 0.7 gram after fungus exposure. A weight loss of 0.7-0.8 gram was common to the series except for the Series II samples, which were started at a later date so that perhaps the wood-attacking fungus was not as effective in this batch, or the second batch survived in a dryer condition before weighing and testing.

To oversimplify the data, all treatments were very effective versus the control (-12). Even a plain polyimide coating (-8) is good. The copper (-10) and propyl p-hydroxybenzoate did show somewhat better results versus the coated control (-8) without fungicide.

Selected coated unimpregnated blocks were leached for one month immersed in running water, dried at room temperature for four days, and additionally soaked in running water for one month (total of two months in water); followed by drying and fungus exposure. Table 11 presents the results.

TABLE 11

Effect of Fungus Exposure on Water-Soaked, Coated Wood

Experiment Number	Fungicide in Coating	Weight Loss (g)		Growth of Fungus on Surface (1)	Soil Rating (2)
		Series	Avg		
4539-2	Trichlorophenol-formaldehyde	0.16, 0.18	0.17	1, 0	3, 1
4539-3	Propylhydroxybenzoate	0.22, 0.17	0.20	1, 0	3, 2
4539-5	Pentachlorophenol	0.21, 0.19	0.20	1, 0	2, 2
4539-10	Copper - reacted in	0.19, 0.17	0.18	1, 2	1, 3
4539-8	None - control	0.21, 0.19	0.20	1, 0	3, 1

(1) Scale of 0 (little growth) to 10 (luxuriant growth) on surface of block.

(2) Scale of 1 (low growth) to 3 (luxuriant growth) in jar of soil plus fungus.

The weight loss data of the approximately 16-gram blocks do not seem to be significant - every batch of coated samples has its own fairly invariant weight loss, regardless of the experimental variable. Either each batch of the wood-attacking fungi is variable in its ability to grow and attack wood, or some batches of sealed, dried blocks picked up water to varying degrees before being subjected to fungus exposure, drying, and reweighing.

The soil rating is based on the degree of growth in the container. If fungicide leaches out of the coating, one might expect not only to protect the wood block but also to poison the fungus growth in the container. Judging from the results with the 4539-8 control, however, either something fungicidal leaches out of the polyimide itself or the fungicide leaching is not adequate to contribute to a different result versus the control. The ASTM G-21 fungi would normally grow all over the average plastic film.

The 4539-2 chlorophenol/formaldehyde was rated better in Table 11 than the unleached (-2) in Table 10. Either the prolonged water immersion may have hydrolyzed some of the chlorophenol free of polymer attachment or the test rating is variable to at least ± "1". The pentachlorophenol (-5), control (-8), and copper-containing (-10) coated blocks were also somewhat better rated than the unleached blocks of Table 10. The propyl hydroxy benzoate (-3) rating was unchanged. Certainly one may conclude that the two-month leached blocks were not impaired in fungus resistance versus the original blocks or versus an uncoated wood block (-12, -14 - Table 10).

Since the uncoated control lost very little weight, if any, there is some question as to whether or not the ASTM tests are adequate for fir wood. Another approach to effect of fungus, in addition to weight loss, was suggested by Toole, Forest Products Journal 19, No. 10 (October 1969) pp 36-37: Cubes of wood were exposed to fungus and the change in crush strength and modulus versus weight loss was determined.

Accordingly, compressive specimens measuring 1.9 x 1.9 x 4.5 cm were cut along the grain from fungus-exposed and nonexposed blocks measuring 4.5 x 4.5 x 1.9 cm. Quadruplicate specimens aged for two days at 73°F and 50 percent RH were tested according to ASTM D-143 type procedures wherein modulus and compressive strength (load at collapse) were measured at a 1.3 mm per minute loading rate (Instron). Results are presented in Table 12. Any fungus attack

TABLE 12

Effect of Fungus Exposure on Fir Compressive Properties

Experiment Number	Fungicide in Polymer	Wood Impregnant	Wood Not Exposed to Fungus, $(N/m^2) \times 10^{-6}$		Wood Exposed to Fungus, $(N/m^2) \times 10^{-6}$			
					After Coating		After 2 Months of Water Immersion	
			Modulus	Compressive Strength	Modulus	Compressive Strength	Modulus	Compressive Strength
4539-12	(1)	-	5343	43.36	4800	47.91	-	-
4539-14	(2)	-	6274	50.25	4681	49.84	-	-
4539-3	Propylhydroxy-benzoate	-	5984	52.67	5315	52.05	5708	49.77
4539-8	None	-	-	-	-	-	5232	49.36
4539-2	Trichloro-phenol/for-maldehyde	-	-	-	-	-	5322	43.1
4545-1A	Same	Fyrprufe	-	-	6204	50.12	-	-

(1) No coating or impregnation - raw wood

(2) No coating or impregnation, but wood was baked at 200°C as control for coated wood.

could not have been very extensive. The -12 and -14 controls were not any weaker than the control/protected wood. Although the surface of -12 and -14 was subjected to heavy fungus growth, the depth of damage in 10 weeks of fungus exposure was apparently very superficial. These results confirm the low weight loss results.

The modulus of the (-1A) Fyrprufe-impregnated wood was higher than that of the control wood sample (-12) for some reason. The wood baked at 200°C without a coating (-14) was also stiffer than the other samples tested, but this may possibly have been due to inadequate water pickup between the time it was baked and tested.

The basic problem in the area of fungus testing, then, is inadequate exposure in 10 weeks' time. Fungicides will have to be checked over a much longer period of time or with a more porous wood - e.g., pine. The apparent fungicidal nature of the polyimide coating itself (-8) increases the difficulty of screening fungicidal additives.

Fungicide-Polyimide Interaction

The water leaching data - Table 9, page 39 - indicates that the fungicides are not readily removable from the polyimide. It is of interest to know whether the fungicide is merely difficult to remove from the polyimide or whether it is actually partly chemically reacted with the polyimide. Certainly the copper was reacted-in; particles of copper acetate are visible until the reaction is complete.

Since the propylhydroxy benzoate appeared to have a slight edge in the fungicide tests and would probably yield a less acrid smoke than chlorophenol in a mine fire, detailed analytical work was carried forth with the propylhydroxy benzoate.

Infrared -

Polyimide films with and without 5 phr propylhydroxy benzoate were cast and removed from the heating cycle at various times - e.g., 1 hour at 120°C, 1 hour at 120°C plus 1 hour at 150°C, and 1 hour at 120°C plus 2 hours at 200°C. The 2-3 mil films were too thick for IR work but were broken up and run as a salt mull. No difference in the spectra at a given temperature with or without propylhydroxy benzoate was detected. None of the fungicide absorption peaks were strong enough to show through the polyimide spectra.

The experiment was repeated with 20 phr propylhydroxy benzoate fungicide. The presence of the fungicide was detectable at this level - especially at 12.95 microns of benzoate Ø (phenyl) and 8.6 microns of benzoate ØOH. The absorbance at 8.6 and 12.95 microns was divided by the C-C absorbance at 7.3 microns and the data tabulated. Results are shown in Table 13.

TABLE 13

Absorbance Ratio Vs. Bake Temperature
Skybond 703 Plus 20 PHR Propylhydroxy Benzoate

Bake Temperature ($^{\circ}C$)	Absorbance Ratio	
	8.6μ (-OH)	12.95μ (Ø)
120	0.39	0.20
150	0.39	0.19
200	0.165	0.10

The hope was that the data would show propylhydroxy benzoate hydroxyl disappearance while keeping the propylhydroxy benzoate phenyl content, indicating reaction with the hydroxyl group.

At first glance it would appear that the propylhydroxy benzoate is volatilizing at $200^{\circ}C$, since both (-OH) and (Ø) are disappearing. This is not that likely, however; a similar $200^{\circ}C$-baked film with 5 phr benzoate yielded 88 percent leachable benzoate by methanol extraction (see Table 9). Also, the (Ø) lost 50 percent of its absorbance ratio after the $200^{\circ}C$ bake, while the hydroxyl lost 57 percent of its absorbance ratio, indicating that the hydroxyl was disappearing at a faster rate than the propylhydroxy benzoate phenyl group.

The IR data is marginally useful, however, since (1) some volatility cannot be ruled out, (2) 20 phr rather than 5 phr of propylhydroxy benzoate is used to obtain the data with possibly shifted reaction equilibria, and (3) other reactions may be occurring at 200°C which could make the 12.95 micron absorption (Ø) shift elsewhere.

Infrared work with solutions would be more definitive, but the cured polyimide film is no longer soluble. Acid hydrolysis of the film to solubilize it would also hydrolyze the benzoate reaction products.

TGA/DTA -

Films baked at 120°C plus 150°C for 1 hour and also 200°C for 2 hours additionally were subjected to TGA (thermogravimetric analysis) to determine if excessive weight loss occurred. Results are presented in Table 14.

The 200°C propylhydroxy benzoate baked films lost very little weight versus the control, no benzoate, up to 250°C. The 20 phr propylhydroxy benzoate baked solely at 150°C did lose weight versus the 0 phr control - probably indicating unreacted volatile fungicide. (The propylhydroxy benzoate by itself volatilizes substantially in the range of 180-235°C.)

The 200°C baked films with 0 or 5 phr benzoate were, within experimental error, equal in weight loss, indicating that there was either no unreacted benzoate, or that the unreacted benzoate was too soluble in the film to evaporate. One could argue that the 200°C-baked, 20 phr benzoate film loses 11 percent (1.9/16.7) of its original benzoate by 300°C and therefore the method is viable. One could also argue, however, that heating to 300°C only evaporates excessive free benzoate content - e.g., a high percentage of the free benzoate over 7 percent (?) content. Also, the 200°C-baked film data does not tell us how much benzoate was lost, if any, during the 200°C bake cycle. The 150°C-baked films indicate that this 200°C bake cycle loss would be a high figure, but the TGA heating cycle is sufficiently rapid so that the benzoate has more chance to evaporate than react.

Work with DTA (differential thermal analysis) was undertaken in the hope that any unreacted propylhydrozy benzoate in the film would show a sharp endothermic peak at its approximately 100°C melting point while the chemically attached benzoate would not.

TABLE 14

Weight Loss Vs. Temperature

$20^{\circ}C$ Per Minute Heating

PHR/Percent By Weight Propylhydroxy-Benzoate	Highest Bake Temperature (°C)	Percent Weight Loss at				Percent Weight Loss, Benzoate-Control		
		200°C	250°C	300°C	350°C	200°C	250°C	300°C
0 (Control)	150	4.41	11.17	15.98	-	-	-	-
20/16.7	150	6.5	15.94	23.76	-	2.1	4.8	7.8
0	200	1.77	2.60	5.49	7.65	-	-	-
5/4.8	200	1.50	3.01	5.66	7.42	-0.3	0.4	0.2
20/16.7	200	1.34	2.73	7.43	12.0	-0.4	0.1	1.9

Films with 0 and 20 phr propylhydroxy benzoate cured for 1 hour at 120°C plus 1 hour at 150°C and also with 2 hours at 200°C additional were utilized. The 0 and 20 phr benzoate, 200°C-cured film DTA curves (24°C per minute) were largely without character, merely gently undulating curves. The 150°C-cured films yielded curves similar to each other, although the 20 phr benzoate film did have a very slight downward endothermic thrust centering at 65°C.

A finite area could be marked off, based on change of slope, which is attributable to free hydroxy benzoate. The low melting point (65 versus 100°C) is probably caused by admixture with an unreacted polyimide component. The area attributable to propylhydroxy benzoate melting is very small for, probably, 10-15 percent free benzoate in the 150°C-baked film. The 200°C-baked, 20 phr benzoate-containing film did not appear to have any free benzoate by this test (unlikely).

The DTA curves were also used to interpret exotherm (discussed under Flame Tests and Other Tests on the Final Coating - page 51.

Other Tests or Further Testing -

The leaching tests we used may not be definitive of chemical reaction because of the possibility that hydrolysis occurred during leaching at high temperatures. Dry solvents without hydroxyl constituents should be tried.

The TGA data might be more productive if supplemented by weight loss of film during bake data on benzoate and nonbenzoate containing films. DSC (differential scanning calorimeter) curves would be more sensitive than DTA and might be able to show small amounts of free benzoate in the film. Radioactive benzoate could be used to establish whether or not loss of benzoate is occuring during the polyimide cure.

Leaching of fungicide-containing nonreactive films and cured Skybond containing fungicide infused in, after curing, by means of a swelling solvent should cast more light on the reaction between film and fungicide.

THE FINAL PROCESS

Formulation

Pounds	
100	Monsanto Skybond 703 (65 percent solids)
3	Cabot Cab-O-Sil EH-5
103	

Disperse for 5 minutes with a Cowles-type mixer. Add:

3.25	Propyl p-hydroxy benzoate
10	Butyl cellosolve

Stir in for 5 minutes (61.3 percent solids)

Coating

- Dry the beams for 16 hours at 110°C.
- Brush or spray top of beam; invert and place on a jig (e.g., device with nails projecting upward).
- Coat remainder of beam.
- Bake for 1 hour at 120°C plus 1 hour at 150°C (preferably cool between bake cycles).

- Cool for 5 hours. Roll down any blisters with roller.
- Recoat for approximately 6-8 mil coating; bake 120°C, 150°C.
- Bake for 2 hours at 200°C.
- (Alternate - tentative - bake 45 minutes under IR heater.)
- Cool.
- (Alternate - roll coat three sides, bake, cool coat fourth side.)
- (Alternate - spray coat while hanging from clamp.)

Alternative - (Tentative)

Impregnate beam, before coating, with:

25	Urea formaldehyde resin solids
75	Water
1.25	Ammonium diacid phosphate

Other impregnants for fungus and/or flame resistance should also be suitable (tentative).

Dry for 16 hours at 110°C. Sand surface (tentative - there are unresolved adhesion problems with this impregnant).

Proceed with the above polyimide coating.

FLAME TESTS AND OTHER TESTS
ON THE FINAL COATING

Density

The formulated polyimide has a density of 1.18 grams per cc by water immersion methods.

Hardness

The cast, cured polyimide has a Rockwell hardness of M 120.

Mixing, Storage, and Curing Exotherm

The polyimide/Cab-O-Sil/propylhydroxy benzoate mixture appears to be stable for at least three months at room temperature. Refrigerated storage for long periods is preferred.

The DTA curves on polyimide and polyimide/propylhydroxy benzoate mixtures indicate a slight exothermic reaction at temperatures from 100°C (20 phr benzoate) or 75°C (no benzoate), peaking at 145-152°C. The 150°C heated films, as might be expected, have more of an exotherm than the 200°C heated films. At temperatures over 200°C another exothermic reaction starts. The results indicate that the 200°C, 2-hour heating cycle does not fully cure the polyimide.

Heating the polyimide coating for 1 hour at 120°C results in a somewhat tacky coating at room temperature. Heating for 1 hour at 150°C results in a handleable coating. The 2 hours at 200°C bake cycle produces a cured coating that is insoluble in methyl pyrrolidone, although a much prolonged heating time at much higher temperatures could produce a further cure if desired.

More effort could certainly be devoted to the determination of minimum coating thickness for the purpose at hand: minimum oven time, the effect of IR curing methods, maximum filler loading (cost reduction), etc.

Permeability

Water leaching of the propylhydroxy benzoate using refluxing water in a Soxhlet is minimal (Table 9 - 4513-3).

Humidity Resistance

Coated blocks immersed for two months in water did not suffer any loss in resistance to surface growth of fungus (Table 11 - 4539-3).

Strength

The coated timber by ASTM D-143 Compressive Testing did not appear to be adversely affected by coating and curing (Table 12 - 4539-3 versus 4539-12).

Flame Resistance

- Oxygen Index

Ten fir sticks measuring 6.5 x 3.2 x 127 mm, as is, coated with three coats of polyimide/propylhydroxy benzoate, and also preimpregnated with urea formaldehyde and coated with polyimide/propylhydroxy benzoate, were subjected to ASTM 2863 - Oxygen Index. The top of the stick is ignited and the minimum percent oxygen necessary to support combustion is measured. Our results are presented in Table 15.

TABLE 15

Oxygen Index

Experiment Number	Wood Impregnant	Coating	Oxygen Index
5265-2	None	None	24
5267-1	None	Polyimide plus 5 phr propyl-hydroxy benzoate	37
5267-2	Urea Formaldehyde (1)	Same	46

(1) See page 11

Thus it would appear that under mild conditions of ignition and flame propagation, the polyimide-coated and particularly urea formaldehyde impregnated wood is far more flame resistant than untreated wood. The fir is "nonburning" in 19 percent oxygen (air) by this test.

- NBS Smoke Density

A wood square measuring 7.6 x 7.6 cm is placed vertically in a frame in an NBS-Aminco smoke chamber measuring 914 x 914 x 610 mm. The wood square is exposed to a heat source (2.5 watts per square cm flux) while in a flaming and a nonflaming mode. A vertical photometer path is employed for measurement of light absorption. The optical density is continuously recorded to maximum DMC (maximum specific optical density, corrected for the soot accumulation on the photometer window) or for 20 minutes maximum.

Our test results on NBS Smoke Density are presented in Table 16.

TABLE 16

NBS Smoke Density

Experiment Number	Wood Impregnant	Coating	Mode	DMC Range/Av.	Time to Maximum DMC (min.) Range/Av.
5266-1	None	None	Smoldering	352-397/367	10.3-11.4/10.7
			Flaming	90-123/106	11.3-15.4/12.9
5267-1	None	Polyimide plus propylhydroxybenzoate	Smoldering	225-310/255	11.8-12.4/12.0
			Flaming	37-66 / 52	14.5-17.5/15.7
5267-2	Urea Formaldehyde	Same	Smoldering	296-317/307	11.8-20.0/17.0
			Flaming	38-66 / 47	14.0-17.6/16.0

Thus it appears that fir itself is not overly "smoky", even in the smoldering mode (DMC over 300 is undesirable). The polyimide-coated fir was a definite improvement over the uncoated wood - smoldering DMC was below 300; DMC was two-thirds of uncoated wood; flaming DMC was half of uncoated wood. Time to maximum smoking was extended.

The coated urea formaldehyde appeared to increase the smoldering smoke density versus coated unimpregnated wood, although the time to maximum smoke generation was extended. The urea formaldehyde did not affect the flaming mode smoke by this test.

By these results the polyimide coating definitely reduces smoke generation.

<u>Flame Spread - "2-Foot Tunnel"</u>

This test was carried out by Pandel Chemical Company using a 2-foot (61 cm) tunnel with a top frame inclined 22^{o} with the horizontal. The 61 x 5 cm coated or uncoated wood sample is set into the frame and a Terril burner flame with a metered-in natural gas source is impinged on the underside of the sample (at the low end) for 6 minutes. The length of the maximum flame front on the wood surface and time to maximum front is recorded. The After-Flame Time is also recorded (flaming and afterglow after removal of the burner flame). The smoke number is the area under the curve of photocell light transmission loss versus time (4 minutes). Visual observations are also made, every 15 seconds. The flame spread results are generally comparable to the 25-foot ASTM E-84 tunnel oven results*. Table 17 presents test results.

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* Monsanto Chemical Company; Young, et al. Special Report No. 6090 (May 5, 1964). Use of a Small Flame Tunnel in the Laboratory Evaluation of Flame Spread Rating.

TABLE 17

Flame Spread Tunnel Oven Test

Experiment Number	Wood Type	Wood Impregnant	Coating	Time to Maximum Flame Front Length (minutes)	Maximum Flame Front Length (cm)	Flame Spread Rating	After-Flame (sec)	Smoke Number
-	Red Oak	None	None	3.75	43.0	(100)	15	0.105 (Av.)
5266-1	Fir	None	None	3-4	44.5-51.0	111	23-40	0.06 - 0.339
5267-1	Fir	None	Polyimide + benzoate	1.75-3.0	40.6-46.0 (1)	100	29-35	0.065 - 0.065
5267-2	Fir	Urea formaldehyde	Same	3.5-3.75	40.6-46.0 (1)	100	25-36	0.03 - 0.038

(1) Only 11.5 cm of coating burned off.

The flame spread tunnel tests are quite severe, but in a large-scale fire situation with good air supply, the tunnel test is perhaps more apropos. The oxygen index test in this case tells more about resistance to initiation of the burning condition.

The flame spread tunnel results appear to indicate that the polyimide is burned through rapidly and does not afford much protection in this situation. On ther other hand, not much of the polyimide was burned off during the test. Most of the flame spread is apparently due to flammable volatiles given off by the wood where the coating burned through. This particular test is apparently heavily weighted toward wood containing phosphate char-promotor (less flammable volatiles) or toward some sort of insulating coating (asbestos, intumescent, etc.).

The urea formaldehyde similarly does not appear to assist matters under the test conditions. As in the NBS smoke test, the polyimide coating helps to cut the flaming mode smoke evolution. Unlike the NBS test, in the flame spread test the urea formaldehyde reduced the smoke evolution.

COST DATA

Coating cost data was derived using as a "typical" case timber measuring 12" x 12" x 11' (30 x 30 x 307 cm). As a reference point, the present cost of such timber at $160 per 1,000 board feet would be about $21. The present cost of a timber impregnated with a typical fungicidal material would be about $28 ($210 per 1,000 board feet).

The following coating cost calculations (also see Appendix) are based on: (1) a million square feet (92,937 M^2) or 21,739 timbers, (2) 10 million square feet (929,368 M^2) or 217,390 timbers, and (3) 100 million square feet (9.29 MM M^2) or 2.17 MM timbers. Calculations are further based on: the cost of spraying and simple brushing on of 0.125 and 0.25 mm (5 and 10 mil) coatings; plus the use of a conveyor system (Figure 6) or horizontal beam supporting jigs which can be moved by forklift truck.

A ten-year depreciation period for equipment is assumed. Interest on capital and profit is not included. An inexpensive shed is assumed for storage of wood until processed. Exhaust to air is assumed (solvents used are exempt).

Table 18 presents the resultant coating cost calculations in summary.

From these data, it appears that at the 1 MM square foot production level, with least expensive application method, the cost of coating materials at 5 mils of coating thickness is half the cost of coating the timber and two-thirds of the cost at 10 mils thickness. At the 10 MM square foot production level, with least expensive application method, the cost of coating materials at 5 mils of coating thickness is two-thirds of the cost. At the 100 MM square foot production level, with least expensive application method, the cost of coating materials at a 5-mil coating thickness is three-fourths of the cost.

At a 1 MM square foot per year output, the facilities are rather small and a conveyor system wherein the timbers hang from clamps should not be considered unless the plant will likely expand production. At a 10-100 MM square foot per year output, the facilities are in the range where the conveyor system should be considered. The spray method of application would be much less expensive, ordinarily, but the likely polyimide overspray wastage is very expensive unless a way can be found to recover, redilute, balance solvents, and filter the overspray residues.

A 5-mil coating would add about $11-12 to a $21 beam using the present polyimide-fungicide without fillers.

TABLE 18

Coating Cost Calculations

Method	Number of Shifts	Cost ($) Per Square Foot (0.093 M^2)/Cost Per Timber		Number of Coats
		5 Mils (0.127 mm)	10 Mils (0.254 mm)	
Output per year: 1 MM ft^2/92,937 M^2/21,739 timbers 12" x 12" x 11'				
(Materials only)	-	0.17/7.87	0.34/15.74	-
Brush coat/move by hand-jig-forklift	3	0.34/15.70	0.51/23.57	1
Brush coat/move by conveyor system	1	0.62/28.34	-	-
Spray coat/move by hand-jig-forklift	3	-	0.79/36.41	2
Output per year: 10 MM ft^2/929,368 M^2/217,390 timbers 12" x 12" x 11'				
Brush coat/move by conveyor system	3	0.270/12.46	-	-
Brush coat/move by hand-jig-forklift	3	0.299/13.77	-	-
Spray coat/move by hand-jig-forklift	3	0.397/18.29	-	-
Output per year: 100 MM ft^2/9.29 MM M^2/2.173 MM timbers 12" x 12" x 11'				
Brush coat/move by conveyor system	3	0.24/10.88	-	-
Brush coat/move by hand-jig-forklift	3	0.30/13.59	-	-

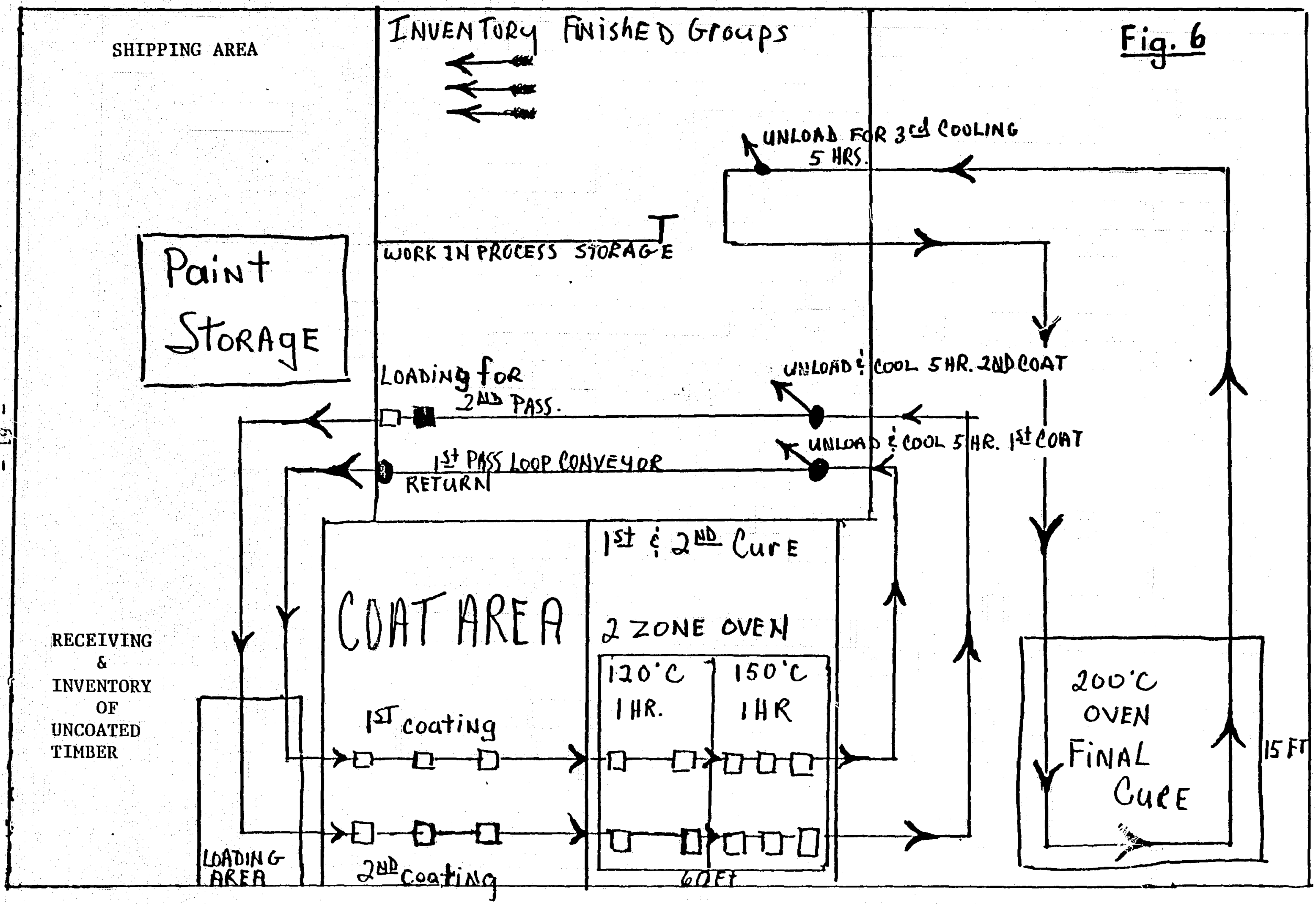
SHIPPING AREA
INVENTORY FINISHED GROUPS
WORK IN PROCESS STORAGE
Paint Storage
UNLOAD FOR 3rd COOLING 5 HRS.
LOADING FOR 2ND PASS.
UNLOAD & COOL 5 HR. 2ND COAT
UNLOAD & COOL 5 HR. 1st COAT
1st PASS LOOP CONVEYOR RETURN
1st & 2ND CURE
2 ZONE OVEN
120°C 1 HR.
150°C 1 HR
COAT AREA
1st coating
2ND coating
RECEIVING & INVENTORY OF UNCOATED TIMBER
LOADING AREA
60 FT
200°C OVEN FINAL CURE
15 FT

Fig. 6

GENERAL CONCLUSIONS

(1) Curable polyimide - e.g., Monsanto Skybond 703 - in thin films was found to be flame resistant, with minimal fumes, in a torch flame. Other materials screened were less desirable.

(2) Coated on fir wood together with 5 phr fungicide, the Skybond resisted relatively brief exposure to a torch, but apparently burned through readily in a tunnel oven type test. Wood preimpregnated with urea formaldehyde yielded similar results.

(3) Polyimide-coated wood generated considerably less smoke versus uncoated wood.

(4) Polyimide-coated wood is more difficult to ignite than uncoated wood (oxygen index).

(5) Polyimide-coated wood (cured for 2 hours at 200°C) was very resistant to fungus growth with and without the presence of a fungicide.

(6) Several fungicides were found to have very low but finite hot-water leaching rates.

(7) The extent of chemical reaction between the fungicide - e.g., propyl-p-hydroxy benzoate - and the polyimide was not satisfactorily defined.

(8) Fungicides tentatively identified as being suitable for baking into polyimide films include: propyl-p-hydroxy benzoate, pentachlorophenol, trichlorophenol, trichlorophenol-formaldehyde adduct, Merck TK-100 benzimidazole, Vanderbilt Ziram, copper salt (acetate), and bis(tributyl tin) oxide.

(9) Infrared curing of the polyimide coating appears to be feasible. This would cause less of a potential problem with overheating of

the wood near the surface and would minimize the heating of any wood impregnant.

(10) Cost considerations will eventually require a 2.5-5 mil polyimide coating with a one-coat application.

SUGGESTED FUTURE WORK

FLAME RESISTANCE

The polyimide is probably sufficiently nonsmoke-generating, but more work should be carried out to provide timber with prolonged resistance to furnace environments. There are four approaches to consider:

(1) Development of a polyimide-based intumescent formulation. A mostly thermoplastic polyimide would probably be necessary. Pioneering development with leach-resistant materials would probably be required.

(2) Small hollow glass bead filler might yield an intumescent type effect. Hydrated aluminum oxide filler might be helpful.

(3) Impregnation of the wood with flame-resistant materials before coating on the polyimide.

(4) From time to time new flame-resistant materials appear, and these should be screened versus polyimide.

FUNGUS RESISTANCE

There are a number of areas to consider:

(1) Before fungicide screening and minimum effective fungicide content can be established, a more definitive fungus test for fir must be established. Approaches to be considered include:

- The use of a more susceptible wood for accelerated testing - e.g., pine.
- The use of a 12-month fungus exposure for fir - probably on a 1 cm cube of coated wood.
- The use of an ASTM G-21 type test wherein the halo of dead fungus around a small piece of polyimide-fungicide film is measured.

(2) The effect of IR cure of the polyimide, which appears to be more efficient with regard to leachable content, should be ascertained for fungus resistance.

(3) Fungicides should be screened again with the improved test, assuming one can be developed.

(4) Combinations of fungicides may be even more effective.

(5) More work should be undertaken to determine if the fungicides of interest are reacted-in or merely dissolved in the film.

(6) The effect of level of fungicide should be investigated.

(7) The effect of baking time/temperature on leachability and fungicidal activity should be determined.

(8) Treated fir beams should be placed in known "bad" areas of mines where fungus-caused rot is a problem. After some years of exposure, pieces should be removed for physical tests.

(9) Impregnation of the beam with a good or mediocre fungicide system, along with any flame-retardant system, should be undertaken as one of the experiments in any long-term aging program in a mine.

COST/PROCESSING IMPROVEMENTS

More work is needed on cost improvement methods. Suggestions are:

(1) The minimum effective thickness for solid coating and intumescent coating should be determined. The polyimide coating material is expensive.

(2) A method is needed to apply the above minimum coating thickness in one coat. In this particular instance, multiple coatings are quite expensive. Spray coating would be very economical if a way could be found to collect and resolvate the overspray properly.

(3) A black or dark pigmentation would be more effective for IR (infrared) cure systems. Type and quantity of black should be investigated. Minimum heating time/temperature to assure adequate cure should be determined.

(4) Fillers in the coating would reduce cost and possibly increase flame resistance. Hollow spheres have been discussed under Flame Resistance, above.

(5) The minimum bake time at 120°C and 150°C, using minimum effective coating thickness, should be determined.

APPENDIX

Cost Calculations

PRELIMINARY ESTIMATE

COATED BEAMS FOR MINE TIMBER
COMPARATIVE ANNUAL OPERATING COSTS

1. RAW MATERIALS

Formula	Pounds	Unit Price $/Pound	Total Cost $/Pound
Skybond 703 (65% TS)	100.00	3.50	350.00
Cab-O-Sil	3.00	1.58	4.74
Propyl-p-hydroxy benzoate	3.25	2.95	9.59
Butyl Cellosolve	10.00	0.39	3.90
TOTAL	116.25		386.23

Cost of raw materials = 368.23/116.25 = $3.17/pound

Loss in handling = 3%

Raw material cost = 3.17 + 0.09 = $3.26/pound (wet) or
$7.19/kilo (wet)

2. MATERIAL USAGE

One timber is typically 12" x 12" x 11' (30 x 30 x 307 cm). Thus, Total surface area of one timber = 46 ft^2 (4.27 square meter).

The final density of the coating = 1.18 g/cc.

For 10-mil (0.254 mm) thickness: 2.8 lb dry; 4.6 lb wet.

For 5-mil (0.127 mm) thickness: 1.4 lb dry; 2.3 lb wet.

A. If brushed on, estimated material loss = 5%.

(4.6 lb/46 ft^2 surface = 0.1 lb/ft^2)	-	4.60 lb
	5% loss	0.23 lb
		4.83 lb

Thus, at 10-mil thickness, 4.83 pounds (wet) needed for one timber (46 square feet); and at 5-mil thickness, 2.42 pounds (wet) needed.

Raw material cost for one timber =

At 10 mils - $15.74 At 5 mils - $7.87

B. If sprayed on, estimated loss = 50%.*

Thus, raw material cost for one timber =

At 10 mils - $29.92 At 5 mils - $14.96

* Unless effort is made to recover a part of the overspray.

C. Roller coater with brush touch-up: identical to A, above.

3. DIRECT LABOR

A. To mix the coating material -

Mix in 55-gallon drums with a Cowles type mixer. Assume approximately 136 kilos (300 pounds) batch size per drum - one batch mixed while the other is weighed out. The 300 pounds are sufficient to coat some 60 timbers at 10 mils, or 120 timbers at 5 mils.

Time to make one batch: 60 minutes

B. To apply coating -

	Minutes Per Timber (46 Ft^2) 5-Mil Coating Thickness: One Coat	Two Coats
(1) By Brush -		
Dry timber; put in and remove from oven. Place on jig with spikes.	6	6
Assume 2.5 min. to coat one side; thus 10 min. for 4 sides. Assume 1 min. for one end; thus 2 min. for 2 ends. Total time to coat total surface:	12	12
To cure coating, put jig with several beams in and remove from oven; assume 5 min. for one operation, thus 10 min. for total cycle.	10	10
Same as above for second coat; 12 min. for coating plus 10 min. for curing.	--	22

	Minutes For Timber (46 Ft^2) 5-Mil Coating Thickness	
	One Coat	Two Coats
(Brought forward)	28	50
Move from 150^{o}C oven to receive final cure in 200^{o}C oven, and remove from oven for cooling.	10	10
Total coating/curing cycle, including proportional time for mixing the coating material (1 minute):	39	61
(2) By spraying -		
Dry timber; put in and remove from oven.	6	6
Assume 80 seconds for 4 sides and 20 seconds to spray 2 ends	1.5	1.5
Same for second coat	-	1.5
To cure coatings, identical to (1) above.	10	20
Total coating/curing cycle, including proportional time for mixing the coating material (1 minute):	18.5	30

4. ENERGY (UTILITIES)

Parameters:	Heat of Vaporization Calories/g	Btu/lb
Methyl pyrolidone	127.3	230
Butyl Cellosolve	88.4	159

In 116 pounds of solution:

35 lb of methyl pyrolidone:	35 x 230	= 8,050 Btu
10 lb of butyl cellosolve:	10 x 159	= 1,590 Btu
Total		9,640 Btu

Thus, 116 pounds of wet coating material require 9,640 Btu's. For a 10-mil thickness, 0.1 pound of wet coating material is needed. Thus, the Btu requirement is:

$$\frac{9{,}640 \times 0.1}{116} = 8.310 \text{ Btu/ft}^2$$

For a 5-mil thickness the Btu requirement is one-half, or 4.155 Btu/ft^2.

The coating film, presently, has to be heated to 120°C (1 hour), then to 150°C (1 hour), then cooled and cured at 200°C (2 hours).

$$T_1 = 20^\circ C \text{ to } 120^\circ C = 100^\circ C$$
$$T_2 = 120^\circ C \text{ to } 150^\circ C = 30^\circ C$$
$$T_3 = 20^\circ C \text{ to } 200^\circ C = 180^\circ C$$

Specific heat of wood = 0.42 calories/gram/$^\circ$C.

Average density of wood = 7.5 grams/cubic inch, 7.5 grams/16.4 cc, 0.45 grams/cc.

One timber - 132" x 12" x 12"/19,008 cubic inches = 142,560 grams.

One calorie - 0.003968 Btu, or 1 Btu = 251 calories.

To heat wood -

From 20°C to 120°C: 0.42 x 142,560 x 100 = 5,987,520 calories/timber (46 ft^2)

From 120°C to 150°C: 0.42 x 142,560 x 30 = 1,796,256 calories/timber (46 ft^2)

From 20°C to 200°C: 0.42 x 142,560 x 180 = 10,777,536 calories/timber (46 ft^2)

	Btu/ft^2
One cycle to heat to 120°C, then 150°C:	
5,987,520 calories, or 23,854 Btu/46 ft^2	518
1,796,256 calories, or 7,156 Btu/46 ft^2	155
Total	673
To heat from 20°C to 200°C:	
10,777,536 calories, or 42,938 Btu/46 ft^2	933

Because of the low energy requirement to evaporate the solvents, there is little difference between the case of 10-mil versus 5-mil coating thickness. An average of 6 Btu/ft^2 is added to the energy needed to heat the wood to the required temperatures:

One cycle of $120^{o}C/150^{o}C$ needed for one coat, and one cycle at $200^{o}C$ =

$$673 + 933 + 6 = 1{,}612 \text{ Btu/ft}^2$$

Two cycles of $120^{o}C/150^{o}C$ needed for two separate coats, and one cycle at $200^{o}C$ =

$$(2 \times 673) + 933 + 6 = 2{,}285 \text{ Btu/ft}^2$$

Based on similar type ovens, the pattern of heat losses compared to the needed energy requirement of the product is:

		Percent
Product		35
Fixtures	18	
Oven losses	37	65
Make-up air	10	
Total		100

This, in our case, would mean:

Percent	System Use of Btu/Ft^2 One Coat	Two Coats
35	1,612	2,285
65	4,605	6,528
100	6,217 *	8,813 *

* No heat loss is considered for one-hour heating periods since this is compensated for by starting with a pre-heated oven from batch to batch.

5. EQUIPMENT

A. Move timbers by hand jig and forklift truck -

Capital gross estimate to produce 1MM and 10 MM ft^2 per year, approximately:

	$
Paint area, including mixing equipment and forklift truck(s)	35,000
Metal jigs with spikes, 60 x $100	6,000
Two ovens for 120°C/150°C cycle and one oven for 200°C treatment, each oven 15 feet long	45,000
	86,000
Installation	50,000
Engineering	20,000
Total investment	156,000

B. Move timbers by conveyor system (see Figure 6, page 61)

Paint area, including mixing equipment and forklift truck	40,000
Two 2-zone ovens	60,000
One 1-zone oven (final cure)	60,000
Conveyor, 2 loops (800 feet)	160,000
Conveyor, 1 loop (300 feet)	60,000
	380,000
Installation	166,500
Engineering	80,475
Total investment	626,975

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 5-mil coat

Process: Coat by brush/move by hand-jig-forklift truck

Output/Year: 1 MM square feet (21,739 timbers)

Operating Hours/Year: 6,000

	Quantity	Units	Unit Price ($)	$/Year
Raw Materials: 2.42 lb/timber (46 ft^2)	52,500	Lbs	3.26	171,150
Utilities (Energy): Gas	6,217 MM	Btu	1.75/1 MM	10,879
Direct Labor:* 39 min./timber = 0.65 hr/46 ft^2	14,130	Hrs	6.50/4.50	75,585

Variable Manufacturing Cost, Subtotal	257,614
Plant Overhead, Including Indirect Labor (70% of Direct)	52,909
Maintenance Supplies (4% Equipment)	6,240
Insurance and Property Taxes (2% Equipment)	3,120
Depreciation of Equipment (10 years)	15,600
Space Charges (as rented) at $5.90/$Ft^2$ - 1,000 ft^2	5,900
Fixed Manufacturing Cost, Subtotal	83,769
Total Manufacturing Cost	341,383

Unit Cost:		
	$/Mine Timber	15.70
	$/$Ft^2$ of Mine Timber	0.341

*Per Shift: 1 operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 10-mil coat

Process: Coat by brush; move by hand-jig-forklift truck

Output/Year: 1 MM square feet (21,739 timbers)

Operating Hours/Year: 6,000

	Quantity	Units	Unit Price ($)	$/Year
Raw Materials: 4.83 lb/timber ($46\ ft^2$)	105,000	lbs	3.26	342,174
Utilities (Energy): Gas	6,217 MM	Btu	1.75/1MM	10,879
Direct Labor:* 39 min./timber = 0.65 hr/$46\ ft^2$	14,130	Hrs	6.50/4.50	75,595
Variable Manufacturing Cost, Subtotal				428,638
Plant Overhead, Including Indirect Labor (70% of Direct)				52,909
Maintenance Supplies (4% Equipment)				6,240
Insurance and Property Taxes (2% Equipment)				3,120
Depreciation of Equipment (10 years)				15,600
Space Charges (as rented) at $\$5.90/Ft^2$ - 1,000 ft^2				5,900
Fixed Manufacturing Cost, Subtotal				83,769
Total Manufacturing Cost				512,407
Unit Cost: $/Mine Timber			23.57	
$\$/Ft^2$ of Mine Timber			0.512	

*Per Shift: operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 5-mil coat

Process: Coat by brush; move by conveyor system

Output/Year: 1 MM ft^2 (21,739 timbers)

Operating Hours/Year: 2,000

		Quantity	Units	Unit Price ($)	$/Year
Raw Materials:	2.42 lb/timber (46 ft^2)	52,500	Lbs	3.26	171,150
Utilities (Energy):	Gas	6,217 MM	Btu	1.75/1 MM	10,879
	Electricity (75 hp)	335,700	Kwh	0.035	11,749
Direct Labor:* 12 min./timber to coat, rest on conveyor line		10,349	Hrs	6150/4.50	50,570

Variable Manufacturing Cost, Subtotal	244,348
Plant Overhead, Including Indirect Labor (70% of Direct)	35,399
Maintenance Supplies (4% Equipment)	25,079
Insurance and Property Taxes (2% Equipment)	12,539
Depreciation of Equipment (10 years)	62,697
Space Charges (as rented) at $5.90/$Ft^2$ - 40,000 ft^2	236,000
Fixed Manufacturing Cost, Subtotal	371,714
Total Manufacturing Cost	616,062

Unit Cost:	$/Mine Timber	28.34
	$/$Ft^2$ of Mine Timber	0.616

*Per Shift: 1 operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - Two 5-mil coats

Process: Coat by spray; move by hand-jig-forklift truck

Output/Year: 1 MM square feet (21,739)

Operating Hours/Year: 6,000

	Quantity	Units	Unit Price ($)	$/Year
Raw Materials: 2 x 4.60 lb/46 ft^2	200,000	Lb	3.26	652,000
Utilities (Energy): Gas	8,813 MM	Btu	1.75/1 MM	15,422
Direct Labor:* 30 min./timber = 0.50 hr/46ft^2	10,869	Hrs	6.50/4.50	54,910
Variable Manufacturing Cost, Subtotal				722,332
Plant Overhead, Including Indirect Labor (70% of Direct)				38,437
Maintenance Supplies (4% Equipment)				6,240
Insurance and Property Taxes (2% Equipment)				3,120
Depreciation of Equipment (10 years)				15,600
Space Charges (as rented) at $5.90/$Ft^2$ (1,000 ft^2)				5,900
Fixed Manufacturing Cost, Subtotal				69,297
Total Manufacturing Cost				791,629
Unit Cost: $/Mine Timber			36.41	
$/$Ft^2$ of Mine Timber			0.791	

*Per Shift: operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 5-mil coat

Process: Coat by brush; move by conveyor system

Output/Year: 10 MM square feet (217,390 timbers)

Operating Hours/Year: 6,000

	Quantity	Units	Unit Price ($)	$/Year
Raw Materials: 2.42 lb/timber ($46\ ft^2$)	525,000	Lbs	3.26	1,711,500
Utilities (Energy): Gas	62,170 MM	Btu	1.75/1 MM	108,790
Electricity	1,200,000	Kwh	0.035	42,000
Direct Labor:* 12 min./timber to coat rest on conveyor line	61,490	Hrs	6.50/4.50	300,705

Variable Manufacturing Cost, Subtotal	2,162,995
Plant Overhead, Including Indirect Labor (70% of Direct)	210,493
Maintenance Supplies (4% Equipment)	25,079
Insurance and Property Taxes (2% Equipment)	12,539
Depreciation of Equipment (10 years)	62,697
Space Charges (as rented) at $\$5.90/Ft^2$ ($40,000\ ft^2$)	236,000
Fixed Manufacturing Cost, Subtotal	546,808
Total Manufacturing Cost	2,709,803

Unit Cost:	\$/Mine Timber	12.46
	$\$/Ft^2$ of Mine Timber	0.270

*Per Shift: operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 5-mil coat

Process: Coat by brush; move by hand-jig-forklift truck

Output/Year: 10 MM square feet (217,390 timbers)

Operating Hours/Year: 6,000

		Quantity	Units	Unit Price ($)	$/Year
Raw Materials:	2.42 lb/timber ($46\ ft^2$)	525,000	Lbs	3.26	1,711,500
Utilities (Energy):	Gas	62,170 MM	Btu	1.75/1 MM	108,790
Direct Labor:*	39 min./timber = 0.65 hr/46 ft^2	141,300	Hrs	6.50/4.50	647,850

Variable Manufacturing Cost, Subtotal	2,468,140
Plant Overhead, Including Indirect Labor (70% of Direct)	453,495
Maintenance Supplies (4% Equipment)	6,240
Insurance and Property Taxes (2% Equipment)	3,120
Depreciation of Equipment (10 years)	15,600
Space Charges (as rented) at $5.90/$Ft^2$ (8,000 ft^2)	47,200
Fixed Manufacturing Cost, Subtotal	525,655
Total Manufacturing Cost	2,993,795

Unit Cost: $/Mine Timber 13.77

$/$Ft^2$ of Mine Timber 0.299

*Per Shift: operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 5-mil coat

Process: Coat by spray; move by hand-jig-forklift truck

Output/Year: 10 MM square feet (217,390 timbers)

Operating Hours/Year: 6,000

	Quantity	Units	Unit Price ($)	$/Year
Raw Materials: 4.60 lb/46 ft^2 Timber	1,000,000	Lbs	3.26	3,260,000
Utilities (Energy): Gas	62,170 MM	Btu	1.75/1 MM	108,790
Direct Labor:* 18.5 min/timber = 0.31 hr/46 ft^2	67,391	Hrs	6.50/4.50	315,250
Variable Manufacturing Cost, Subtotal				3,684,040
Plant Overhead, Including Indirect Labor (70% of Direct)				220,675
Maintenance Supplies (4% Equipment)				6,240
Insurance and Property Taxes (2% Equipment)				3,120
Depreciation of Equipment (10 years)				15,600
Space Charges (as rented) at $5.90/$Ft^2$ (8,000 ft^2)				47,200
Fixed Manufacturing Cost, Subtotal				292,835
Total Manufacturing Cost				3,976,875

Unit Cost: $/Mine Timber 18.29

$/$Ft^2$ of Mine Timber 0.397

*Per Shift: operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 5-mil coat

Process: Coat by brush; move by conveyor system

Output/Year: 100 MM square feet (2,173,900 timbers)

Operating Hours/Year: 6,000

	Quantity	Units	Unit Price ($)	$/Year
Raw Materials: 2.42 lb/timber ($46\ ft^2$)	5,250,000	Lbs	3.26	17,115,000
Utilities (Energy): Gas	621,700 MM	Btu	1.75/1 MM	1,087,900
Electricity	2 MM	Kwh	0.035	70,000
Direct Labor:* 12 min./timber to coat rest on conveyor line	476,900	Hrs	6.50/4.50	2,182,050
Variable Manufacturing Cost, Subtotal				20,454,950
Plant Overhead, Including Indirect Labor (70% of Direct)				1,527,435
Maintenance Supplies (4% Equipment)				126,000
Insurance and Property Taxes (2% Equipment)				63,000
Depreciation of Equipment (10 years)				315,000
Space Charges (as rented) at $\$5.90/Ft^2$ - 200,000 ft^2 **				1,180,000
Fixed Manufacturing Cost, Subtotal				3,211,435
Total Manufacturing Cost				23,666,385

Unit Cost: $/Mine Timber 10.88

$\$/Ft^2$ of Mine Timber 0.236

*Per Shift: operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

** Five times that needed for 10 MM ft^2.

PRELIMINARY MANUFACTURING COST ESTIMATE

Product: Coated Beams for Mine Timbers - One 5—mil coat

Process: Coat by brush; move by hand-jig-forklift truck

Output/Year: 100 MM square feet (2,173,900 timbers)

Operating Hours/Year: 6,000

	Quantity	Units	Unit Price ($)	$/Year
Raw Materials: 2.42 lb/timber (46 ft^2)	5,250,000	Lbs	3.26	17,115,000
Utilities (Energy): Gas	621,700 MM	Btu	1.75/1 MM	1,087,900
Direct Labor:* 39 min./timber = 0.65 hr/46 ft^2	1,413,000	Hrs	6.50/4.50	6,394,500
Variable Manufacturing Cost, Subtotal				24,597,400
Plant Overhead, Including Indirect Labor (70% of Direct)				4,476,150
Maintenance Supplies (4% Equipment)				49,920
Insurance and Property Taxes (2% Equipment)				24,960
Depreciation of Equipment (10 years)				124,800
Space Charges (as rented) at $5.90/$Ft^2$ - 48,000 ft^2 **				283,200
Fixed Manufacturing Cost, Subtotal				4,959,030
Total Manufacturing Cost				29,556,430

Unit Cost:	$/Mine Timber	13.59
	$/$Ft^2$ of Mine Timber	0.295

*Per Shift: operator(s) at $6.50 per hour, including fringe benefits; others are helpers at $4.50 per hour including fringe benefits.

** Eight times that needed for 10 MM ft^2.